

**PROCEEDINGS OF THE
ELEVENTH ARCTIC AND
MARINE OIL SPILL PROGRAM
TECHNICAL SEMINAR**

**COMPTES-RENDUS DE
COLLOQUE TECHNIQUE
DE PROGRAMME DE LUTTE
CONTRE LES DEVERSEMENTS
D'HYDROCARBURES DANS L'ARTIQUE**



**JUNE 7-9, 1988
VANCOUVER, BRITISH COLUMBIA**

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PROCEEDINGS

**Eleventh Arctic and Marine Oilspill
Program Technical Seminar**

**June 7-9, 1988
Sheraton Landmark Hotel
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Seminar sponsored by

**Technology Development and
Technical Services Branch
Environmental Protection
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COMPTES RENDUS

**Colloque technique de programme
de lutte contre les déversements
d'hydrocarbures dans l'arctique**

**7 au 9 juin, 1988
Hotel Sheraton Landmark
Vancouver (Colombie-Britannique)**

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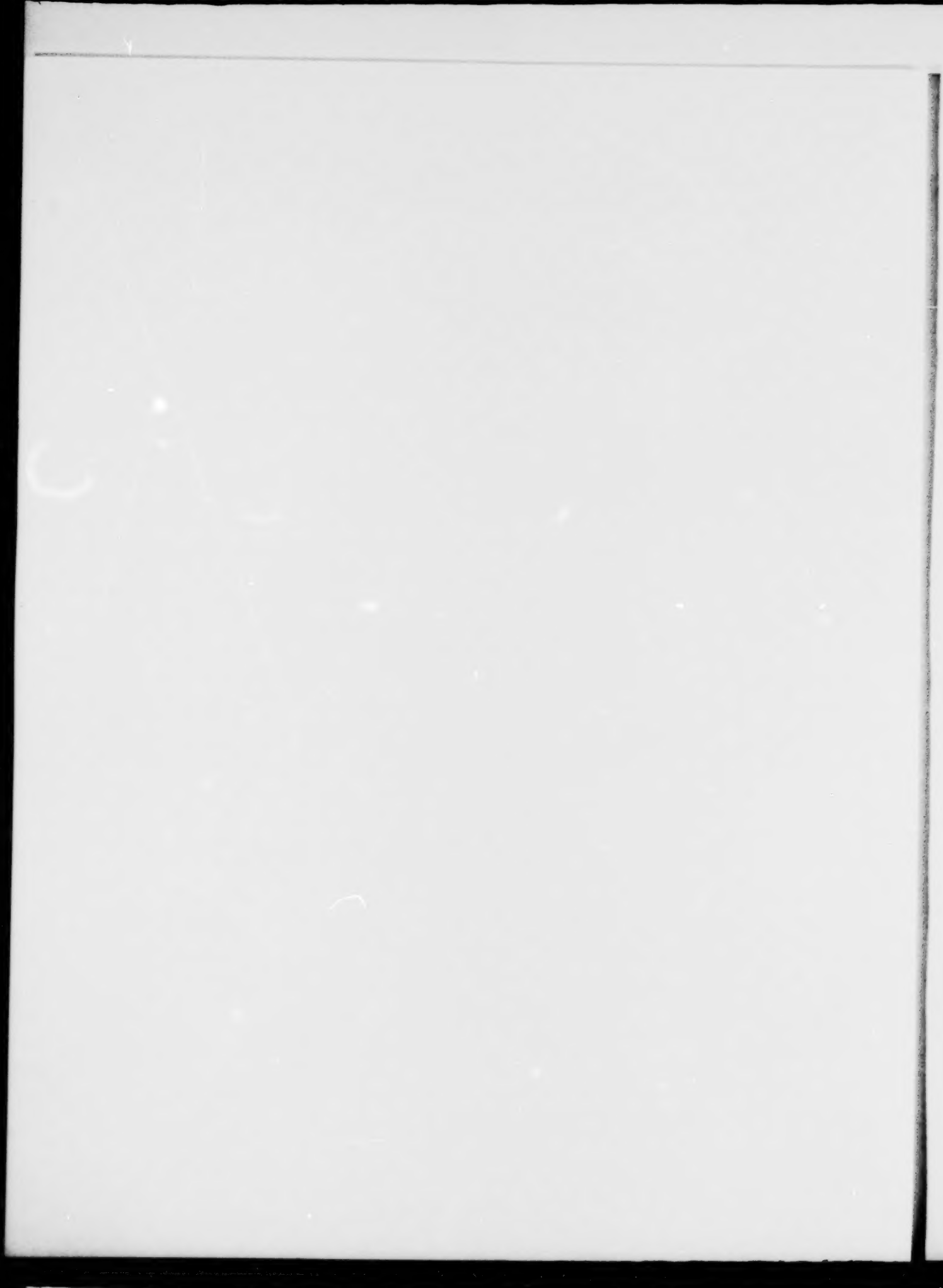
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THE ROLE OF OCEANIC FRONTS IN OIL SPILL DISPERSION AND FOR OIL SPILL RESPONSE PLANNING IN THE COASTAL ZONE

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INTRODUCTION

Over the past decade coastal and marine oil spill response plans have become more sophisticated by the inclusion of data on many aspects of the physical process environment. For example, booming strategies at inlets are being designed to allow for variations in the direction and velocity of tidal currents at different locations and at different stages of the tides (Foget et al., 1979; Owens et al., 1985; Paskewich et al., 1981). Also the role of winds and surface currents in the movement and dispersion of surface slicks has been defined and modeled (e.g. N.A.S., 1985; Spaulding, 1988). One physical element that, to date, has been missing from trajectory modeling and from response plans is the role of oceanic and nearshore fronts. The role of fronts was described by Murray (1982) and this discussion considers some of the applications of this knowledge to coastal response planning.

FORCES THAT AFFECT THE MOVEMENT OF OIL ON THE SEA SURFACE

The primary forces that control the transport and dispersion of oil on the water surface are the movement of air above the oil (wind) and the movement of water below the oil (currents). The relationship between these two variable factors is described by many studies. Winds can be generated by a range of driving forces that include planetary circulation, regional weather systems, pressure gradients or local sea breezes (Figure 1). Currents are generated by many factors that include oceanic circulation, tidal forces, winds, density gradients and sea surface slopes. The interaction between these factors is often complex but the net result is that oil is transported and dispersed. In some cases, predictive models can accurately forecast the movement of a spill but, where the data base is inadequate or incomplete, they may prove to be of little value.

Other factors that must be considered would include local conditions, such as wave reflection from headlands and river discharge, and the possibility of the slick sinking and being moved subsurface. In addition to all of these components it is necessary to add those physical oceanographic elements that may affect surface, or subsurface, movement and spreading. These elements are associated with density, temperature or salinity gradients or fronts that exist where two or more water bodies meet.

THE CHARACTER AND ROLE OF FRONTS

The zone of contact between two water masses of sharply differing densities, salinities or temperatures is referred to as a "front". The basic physical processes controlling fronts in ocean and coastal waters are much the same as those involved in the more familiar cold and warm fronts in the atmosphere. Fronts are particularly common in coastal waters where they are associated with the outflow of rivers and estuaries, with topographically-induced upwelling at capes and headlands, and with larger scale wind-

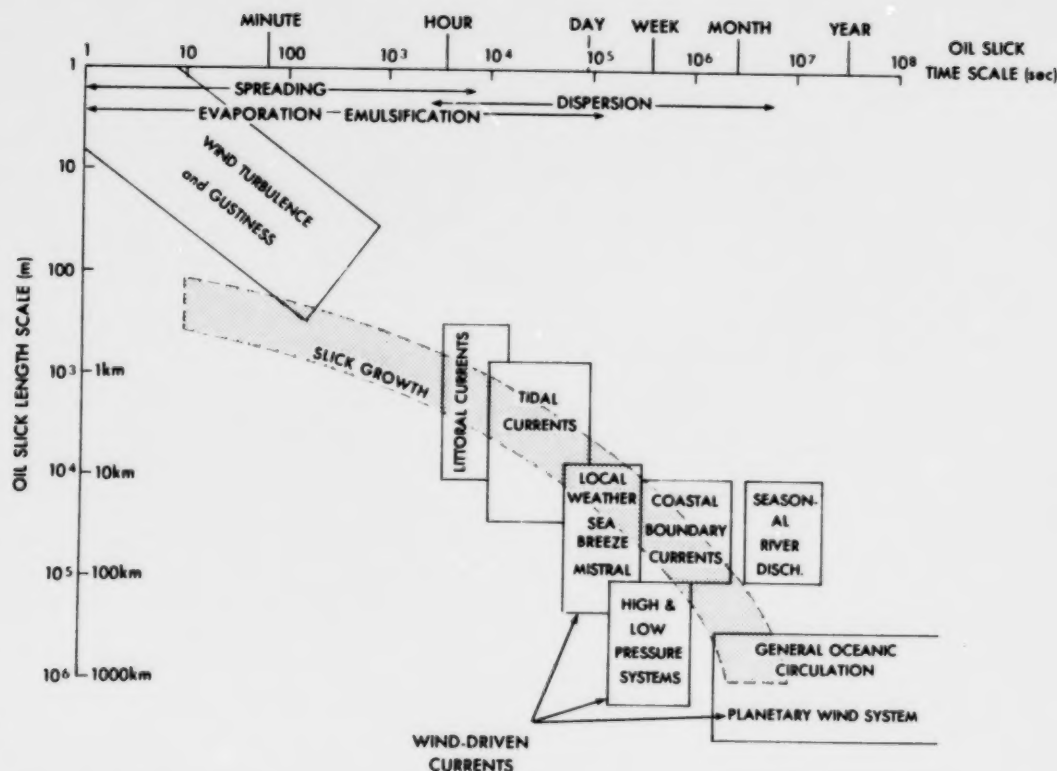


Figure 1. Schematic illustration of the time and length dependence of oil slick growth on physical processes (from Murray, 1982)

induced upwelling that is common off the west coasts of continents at all latitudes. Another type called "shallow sea fronts" is common in shallow seas and bays where bathymetric variability and strong tidal mixing coexist.

The complex velocity field associated with fronts makes them critically important in oil spill dispersion. Current velocities in water masses on both sides of the front converge toward the frontal axis carrying with them all manner of flotsam and especially buoyant, spilled oil. In the immediate vicinity of the front horizontal currents are very strong and turn to move parallel to the front. At the same time, both water masses move vertically downward with the denser water mass diving under the lighter water mass. Buoyant oil, influenced by the frontal zone, will at first move toward the front and then, unable to cross the front or to sink at the convergence zone, will collect and string out parallel to the front. Thus frontal zones, which are ubiquitous in coastal waters, become large and very efficient traps or natural booms for spilled oil. Data on the presence, location, spatial variability and temporal variability of such fronts is important as they can vary with seasons, wind regimes, daily and fortnightly tidal cycles, and river stages.

Whatever the cause of the density front, the effect is that of a natural barrier that can prevent the oil from moving in a direction that would otherwise take place due to driving forces such as near-surface winds.

EXAMPLES OF DOMINANT FORCES

TORREY CANYON - Winds

The movement of the 1967 spill is an example of the effects of wind on the long-term drift of the slick. The track of the slicks can be directly related to wind shifts, despite strong reversing tidal currents that exceeded 1.0 m/sec in this area. Initially oil moved south, away from the English coast, for 6 days under the influence of winds out of the north. Then a wind shift to the southeast caused newly released oil to be stranded and moved the existing, older, slick into the English Channel. This was immediately followed by another shift and consistent westerly winds for 2 weeks, until winds out of the northeast pushed oil southwards onto the Brittany coast.

ARGO MERCHANT - Winds and Tides

Following the ARGO MERCHANT spill in December 1976, the oil did not make contact with the shoreline and was dispersed into the Atlantic because of "prevailing offshore winds for most of the spill period" (NAS, 1985). The actual movement of the slick was more complex than a simple offshore motion and is an example of the combined effects of wind and tidal currents. The oil initially moved shoreward under the influence of ENE winds and maximum tidal currents that exceeded 1.0 m/sec. The slick turned to the northeast, following a wind shift, but then reversed into the northeast setting wind-generated current as the tide turned. Wind became the dominant force with the passage of 3 strong low-pressure systems through the region during the crucial period when the ship broke up and oil releases were at a maximum. These systems resulted in winds of 20 m/sec and generated currents of 80 cm/sec to move the oil to the east.

AMOCO CADIZ - Winds, Tides, Currents etc. etc.

The spill from the AMOCO CADIZ was near the coast and was characterized by persistent onshore winds. During this incident, nearshore and inner shelf processes played a dominant role in trapping the oil against the shore. Initially, tidal currents, often over 1.0 m/sec, running parallel to the shore carried oil along the coast. The oil was released inside the coastal boundary layer (a wedge of highly stratified water only a few tens of kilometers wide) and the onshore winds resulted in a water-level setup that generated a 50 cm/sec current downwind along the coast. Local physical conditions resulted in a wide range of forces that controlled the movement of the oil. These included zones of flow separation that left some waters oil free, the presence of headland fronts and the unusually high tides, due to shelf (Kelvin) waves in the English Channel. These varied forces precluded the use of standard trajectory and forecasting models (Galt, 1978).

CHEVRON MP-41C - Weather systems and density fronts

An explosion on this offshore production platform, located off the east flank of the Mississippi delta in the Gulf of Mexico, in February 1970 resulted in a steady discharge of more than 1000 bbl/day over a 20-day period. At the time several different water bodies were present in the area. Turbid, cool, river water, during a period of high discharge, contrasted with clear, warm, saline Gulf water so that sharp density fronts formed throughout the area near the major river outlets. The location of these semi-permanent fronts varied under the influence of tidal currents and wind stress. Slicks were driven primarily by wind-generated currents but upon meeting a density front were deflected along or trapped against the fronts. Examples of slick movements are given in Figure 2 that illustrate how density fronts played a role in altering drift patterns. In example C the slick was initially pushed away from Pass A Loutre and Southeast Pass and then later deflected to the southeast, along the density front associated with discharge from South Pass. Example E, of a slick mapped the following day, again shows the deflection caused when the oil reached the Pass A Loutre front. Examples G and H illustrate the effects of a drop in wind velocities after noon on the 15th that resulted in a westerly setting rebound

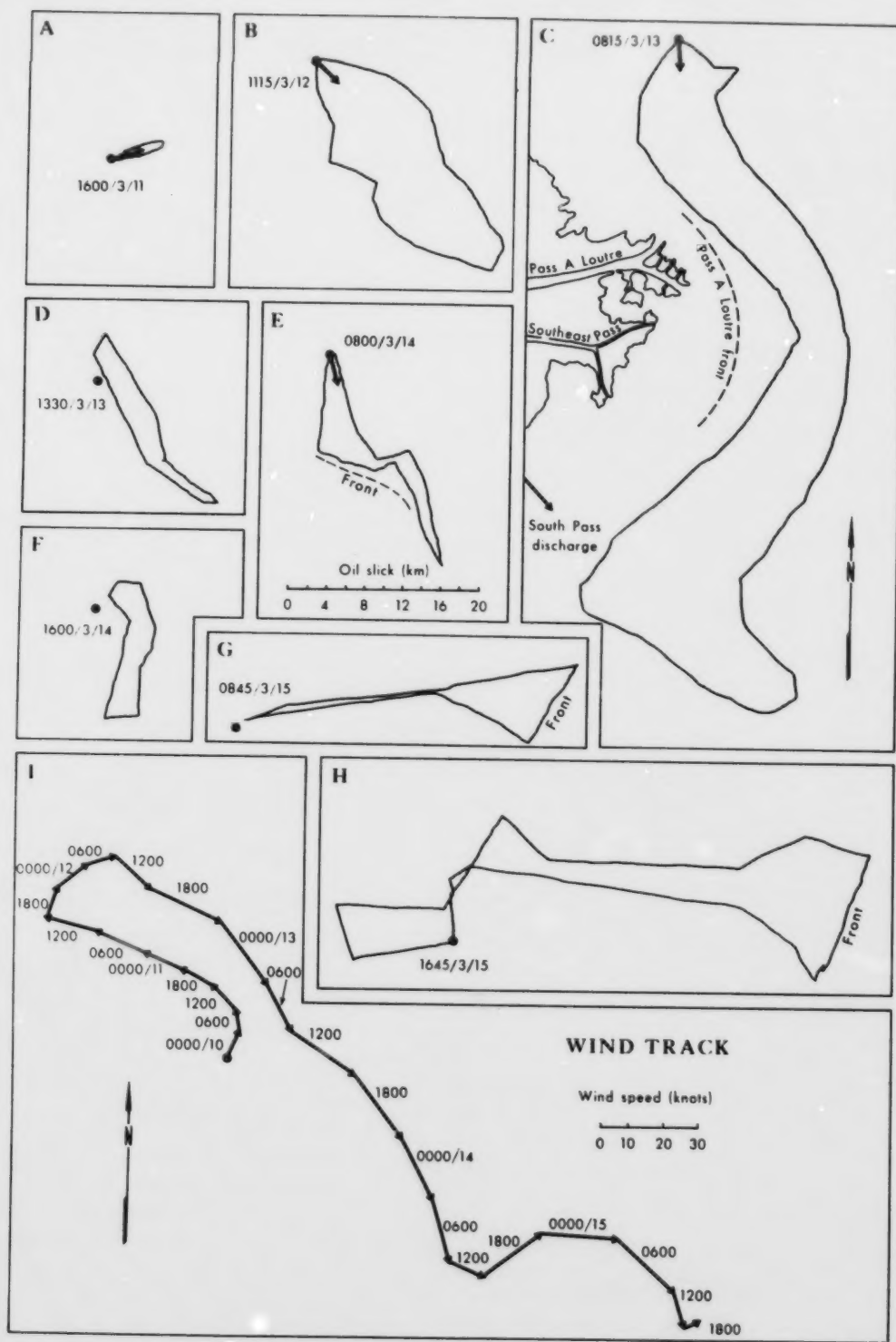


Figure 2. Maps (A through H) of oil slick trajectories from the damaged Chevron platform MP-41C, March 11 to 15, 1970 compared to wind velocities (I) recorded at a nearby (10 km) lightship (from Murray, 1975).

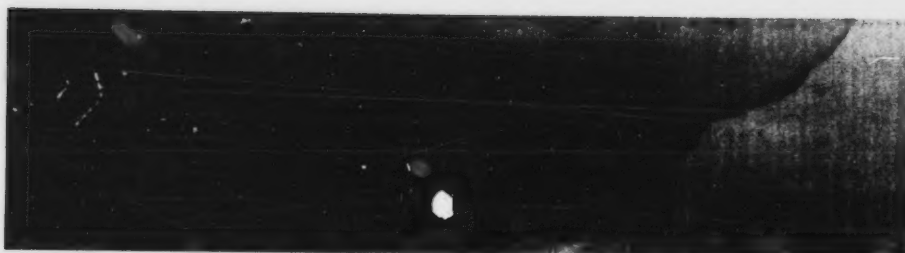


Figure 3. NASA thermal scanner imagery of the slick from the Chevron platform on March 6, illustrating the slick being cutoff by a density front (arrow). The seven white rectangles adjacent to the platform (curved arrow) are barges used to deploy booms across the path of the slick, with obviously little success.

current that abruptly halted the progress of the slick. Figure 3 is a thermal scan image of the slick taken on 16 March that shows the movement of the oil away from the platform (curved arrow) to the north (right). The movement of the oil is truncated by an extensive front and oil is concentrated along the frontal line (arrow). Although winds associated with migrating pressure systems controlled the overall movement of the slicks during this spill, also important in this area was the role of density fronts blocking and realigning slicks to directions different from those of the local winds.

FRONTS - IMPORTANCE AND APPLICATIONS

Fronts are only one of the factors that influence the movement and spreading of oil on the water surface. However, where present they may be the dominant factor. The geographic area where the role of density currents is most likely to be critical is near a river outlet (estuary or delta). In these environments, the meeting of two sharply different water masses (river and oceanic) creates strong fronts that a slick may not be able to cross.

On a regional scale, a study is presently being conducted on the Guyana Current off the north coast of South America to characterize the conditions under which a spill would be affected by the presence of this wide (tens of kilometers), brackish, coastal boundary current that flows northwest from the mouth of the Amazon River. A major offshore spill, from an ocean-going VLCC in transit, may never reach the adjacent coast, despite consistent prevailing onshore winds. If the spill is on the ocean side of the density front it would be deflected alongshore to, eventually, join and mix with the westerly setting Caribbean Current. The presence of the front therefore acts as a natural barrier to protect the coast under most conditions.

At more local scales, the discharge from large (Mackenzie, Yukon, Fraser) and small deltas would act to protect the coastal zone in the vicinity of the river outlets. Usually considered to be both sensitive and vulnerable in all areas, these environments could be considered in more detail to define sections where some natural self-protection exists so that response activities could be focused in other less protected sections. Similarly, within estuarine environments oil could be trapped or deflected to impact one shore rather than another depending upon local tidal- and river-current circulation patterns.

AN EXAMPLE FROM ECLIPSE SOUND, BAFFIN ISLAND, N.W.T.

Eclipse Sound is a large, deep, drowned glacial valley that separates Bylot Island from Baffin Island. On the evening of 13 August 1987 a plume of water was observed to move rapidly to the east along the shoreline adjacent to the settlement of Pond Inlet, on the south shore of the Sound (Figure 4). This plume was on the order of 100m wide and was visibly different from the main water body in the Sound:

- (1) the water colour was lighter (Fig. 4b),
- (2) the surface was calmer (i.e., fewer waves and ripples) (Fig. 4a), and
- (3) ice floes were travelling west to east (whereas ice in the Sound was travelling NE to SW).

The wind at the time was out of the northeast, at an estimated velocity of 15-20 km/hr. The wind was generating local waves on the order of 20-30 cm in height and was driving ice floes from northeast to southwest.

The front was first observed at the west end of the settlement and was visually tracked as it moved alongshore at a rate of between 1.0 and 1.5 km/hr. The plume evidently originated from the Salmon River that is 2.0 km west of the settlement. Within the area of the plume, although the surface was calmer with fewer ripples and small amplitude waves, 10-20 cm high "swell" waves generated in the Sound by the northeast winds were observed that were refracted and broke at the shoreline (Fig. 4a). It appeared that waves were being dampened as the water surface was rougher nearer the leading edge of the plume and became progressively calmer downwind.

Ice floes within the plume were travelling from west to east at a rate faster than the progression of the plume alongshore. They did not cross the outer (seaward) boundary of the plume. As the floes caught up with and approached the leading edge of the plume they were deflected south, towards the shoreline, and collected against the beach (Fig. 4b). Similarly, ice floes that approached the plume out of the east and northeast did not cross the front and were deflected alongshore to the west, never approaching closer than 20 m to the front.

In this example of local coastal oceanography, the presence of these two contrasting water masses would have had a dominant effect on the movement and dispersion of any oil on the water surface at that time. The floes in the plume were being driven at a rate of about 3-5 km/hr into a headwind of greater than 15 km/hr. Floes did not either enter or escape from the plume.

The movement of ice floes can be taken to approximate the general movement of surface oil, were that to have been present at the time. The analogy for an oil spill in this situation is that the fronts which defined the plume would have been a natural barrier that would have either;

- (1) contained the oil within the near-coastal waters and transported it, against the wind, alongshore to contaminate the beach in front of the settlement; or
- (2) protected the shoreline from any oil being carried towards the settlement from a spill in the Sound.

CONCLUSIONS

Regional and local spill response plans should factor in data on fronts, where it is available, in order to take advantage of natural oceanographic processes in the coastal zone. Spill trajectory analysis should include similar knowledge so that projected slicks do not cross fronts that in reality would be a barrier to slick movement. A local study of frontogenesis, frontal movement and frontal dissipation should be assembled for high-risk sensitive areas. In particular, coastal bays, estuaries and deltas are often environments where fronts develop, due to the meeting of high- and low-salinity water masses, and are frequently areas of high sensitivity and vulnerability to spilled oil.



Figure 4. Views to the (a) northwest and (b) northeast at 21:00 on 13 August, 1987 at Pond Inlet, Baffin Island, N.W.T.

(a) shows the coastal plume with ice trapped against the front, and refracted waves out of the northeast at the shoreline. The difference in colour between the two water masses is due to reflectance as the waters of the Sound have a rougher (rippled) surface.

(b) shows the leading edge of the plume, with rougher wave conditions and with Bylot Island in the background. In this case the difference in colour of the two water masses was real, with the plume waters being a lighter shade of blue.

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MODELLING OF OIL SPILLS IN SNOW

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INTRODUCTION

Comprehensive models now exist to predict the movement, fate and behaviour of cold region oil spills on water (e.g., Mackay et al. 1979), on and under ice (e.g., Wotherspoon and Swiss 1985), on land (e.g. S.L. Ross and McBean 1986) and in pack ice leads (S.L. Ross and D.F. Dickins 1987a). This paper describes the development of process equations to predict the fate and behaviour of oil spills on land or ice in or under snow.

Previous Studies

Studies of oil spill processes in snow conditions began in 1972 with experimental spills of Prudhoe Bay crude oil on Arctic snow and ice (McMinn 1972). At about the same time experimental spills of Norman Wells crude oil on freezing water were conducted in winter near Ottawa (Scott and Chatterjee 1972). Data on the effects of snow on weathering processes are available from these tests.

In 1972, 1973 and 1974 twelve experimental spills of about 1 m³ of Norman Wells crude on land were conducted in the N.W.T. Of these, two were conducted in snow conditions. Detailed data on spreading and thermal effects are available from these tests as well as some weathering information. A simple computer model for predicting oil spreading, heat transfer, evaporation and viscosity was also developed (Mackay et al. 1974).

In 1975, during the Balaena Bay study (NORCOR 1975), data on the absorption of snow by oil and the effect of snowfall on oil evaporation were collected using Norman Wells crude as the test oil.

During the winter of 1979/80 two spills of oil took place (one experimental and one accidental). The effects of snow on each are documented (Buist et al 1980; Dickins 1980). Combustion tests with these oil/snow mixtures were also carried out (Energetex 1981).

During the winter of 1980-81 a series of experimental spills of Prudhoe Bay crude on snow and sea ice was conducted. These tests involved spraying hot oil onto the snow to simulate a surface oil well blowout during mid-winter (-23°C) and spring (+4°C). Data on oil/snow interaction were collected over a two week period (Nelson and Allen 1982).

A comprehensive study of oil weathering processes was conducted by the U.S. Coast Guard (Tebeau et al. 1982) during the winters of 1979/80 and 1980/81 using Prudhoe Bay crude oil and No. 2, No. 4 and No. 6 fuel oils. Snow played an integral role in the experimental design. Considerable data on evaporative loss and subsequent property changes were amassed. Significantly, this study used the "evaporative exposure" approach to correlate losses and property changes, thus providing an excellent data set.

Comfort and Purves (1982) reported oil weathering results from a sample collected at the site of the Griper Bay, N.W.T. oil-in-multi-year-ice experiments. They also reported the possibility that particularized oil/snow mixtures could be blown about by high winds.

Although not specifically related to oil spills, two studies in 1985 and 1986 at the University of Toronto contain useful data. The first (Kawamura and Mackay 1985) involved outdoor experiments to determine the evaporation of volatile liquids. One of the experiments involved a toluene/snow mixture and provides useful insights into the processes occurring in evaporation of oil in or under snow. The second involved small scale experiments and modelling of the spread of chemicals on ice and snow (Kawamura et al. 1986). Significantly, this study was the first to develop a spreading model that related to snow properties and did not require the use of an empirical "surface roughness" factor to predict spreading rates.

Finally, two recent studies, though not designed to study snow/oil behaviour fortuitously resulted in data on the subject; the recent experimental spills off Cape Breton (S.L. Ross and D.F. Dickins 1987b) confirmed some of the spreading equations developed by Kawamura et al 1986 for oil in thick brash ice and provided good data on oil weathering in thick brash ice. Outdoor tank tests of oil behaviour in leads shed further light on the absorptive capacity of oil for snow and the effect of snowfall on oil behaviour and weathering (S.L. Ross and D.F. Dickins 1987a).

Study Approach

Prior to the detailed planning of the experiments it was necessary to retrieve, collate and study the considerable body of data already existing on the behaviour of oil in, under or on snow. Table 1 shows such an analysis, for the literature sources discussed previously. It is seen that the effects of snow properties and spill type on spreading and weathering processes, and snow depth on spill weathering have been poorly studied and understood.

Once the key data gaps were firmly identified, small and mid-scale outdoor tests were conducted to collect data on spreading and evaporation. Additional tests were conducted at Arctic locations to evaluate snow drifting as an oil transport mechanism. It was necessary to conduct outdoor tests since it is impossible to create realistic snow indoors or even use real snow indoors since excavation and transportation irrevocably changes its properties.

TABLE 1 – Preliminary Literature Data Analysis

Number of studies in which the parameter
was measured or predicted for its effect on:

<u>Parameter</u>	<u>Oil Spreading</u>	<u>Oil Weathering</u>
snow properties	1	0
snow depth	4	1
oil properties	4	9
oil quantity	6	4
oil thickness	6	2
temperature	3	9
wind speed	0	3
weather	3	3
spill type	1	1

Process equations, based on accepted theory, literature and experimental results were then developed to describe the fate and behaviour of oil on or under snow and on an impermeable surface.

EXPERIMENTAL METHODS

The Test Oil

The crude oil selected for these tests was Mixed Sweet Western, the properties of which are given in Table 2. This particular oil was selected since it is very close in properties to the EPS standard crude and its properties and spill behaviour in cold climates have been extensively studied and are well known (e.g., S.L. Ross and D.F. Dickins 1986; S.L. Ross and D.F. Dickins 1987; S.L. Ross and DMER 1988).

TABLE 2
PROPERTIES OF MSW CRUDE

Density	@	0°C	0.858 g/cm ³
Viscosity	@	0°C	10 mPas
Interfacial Tensions			
air/oil			25.7 mN/m
oil/seawater			19.0 mN/m
oil/water			26.2 mN/m
Pour Point			-8°C
Flash Point			7°C
modified ASTM distillation			T _o = 384.9°K T _g = 539.7°K

Small-Scale Evaporation Studies

Pyrex baking trays containing 1 cm of oil initially filled to various depths with snow were placed in an exposed location near Woodlawn, Ontario for two weeks in February. Three trays were filled with 45 mm of snow of different density (created by manually compressing the snow in two of the trays); two trays were filled with different heights of uncompacted snow (100 mm and 200 mm) and the sixth contained no snow, for a control. Wind speeds and air and oil temperatures were recorded using a remote weather station and thermocouples; data were recorded approximately every three hours on a TRS-80 micro-computer.

Evaporative loss was determined periodically by recovering small (20 ml) samples of oiled snow from the bottom of each tray, carefully melting and decanting the water phase. The oil sample's density was then determined at 0°C using a Parr

densitometer. Evaporative loss was calculated using a verified density/evaporation calibration curve for the MSW oil.

Mid-Scale Spreading and Evaporation Studies

These experiments were conducted at the National Research Council of Canada's Outdoor Manoeuvring Basin in Ottawa during February 1988. Two test spills of about 200 L each of MSW crude were conducted from catwalks above the snow (Figure 1). The oil was released into the snowpack at the centre of each test area and its spreading along four radii monitored by timing the appearance of oil in the bottom of bore holes spaced 30 cm apart (Figure 2). The first test was conducted with virgin snow; the second with snow densified and thickened with snow blown onto the test plot from adjacent areas (Figure 3). Snow properties (density, crystal size, stage of metamorphosis and thickness) were determined using a standard NRC snow kit. Oil samples were collected and analysed as described above to determine evaporation rates.

Small Scale Blowing Snow Tests

A small, portable test kit consisting of three trays (Figure 4) two pre-measured oil samples and sample vials were sent to three Arctic locations to be set up near weather stations to determine if blowing snow transported oil from a surface spill. Arctic locations were necessary for these tests since the extreme cold generates a type of snow not normally found in southern Canada. Oil losses to blowing or drifting snow will be determined by comparing the weight gains and losses of a control tray (no oil) with those of a tray containing oil; corrections for evaporation losses will be made based on oil samples from the third tray to be analyzed as described above. At the time of writing these tests are still ongoing; no results are as yet available.

RESULTS AND DISCUSSION

Spreading of Oil on Snow

Since the literature review yielded several studies on spreading of oil on ice and snow, no additional experimental studies were felt to be necessary. The data of the previous studies was used to develop and confirm a spreading theory for oil on ice or snow.

Theory The theoretical spreading model is based on a balance of forces per unit volume of oil, as used by Fay (1969) in analysing oil spreading on water, modified to reflect the physical situations of oil on snow or ice. The three forces involved in the spreading are gravity, viscous and inertia, the first being a driving force and the latter two resistances. Surface tension forces are neglected since oil on ice or snow inevitably ceases spreading at thicknesses (on the order of 5 mm) much greater than those at which surface tension forces become dominant. The forces can be defined as:

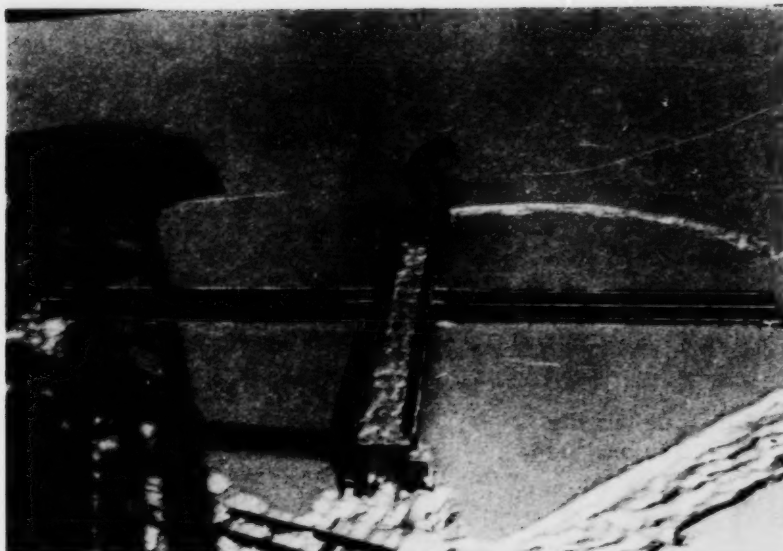


Figure 1 — Mid-scale test site layout



**Figure 2 — Bore holes to monitor
oil spreading beneath snow**



**Figure 3 — Mid-scale test site
with additional snow**

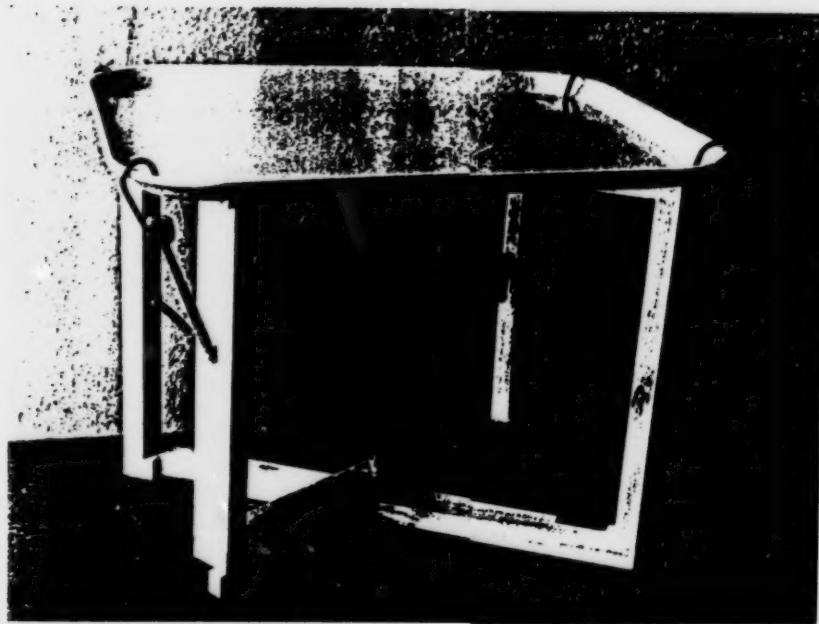


Figure 4 — tray for Arctic tests

	Continuous Source	Instantaneous Spill
Gravity	$= \rho g Q t / r^3$	$= \rho g V / r^3$
Viscous	$= \rho \nu^{1/2} \pi r^3 / Q t^{5/2}$	$= \rho \nu^{1/2} \pi r^3 / V t^{3/2}$
Inertia	$= \rho r / t^2$	$= \rho r / t^2$

where	ρ	= oil density (kg/m ³)
	g	= gravitational acceleration (m/s ²)
	Q	= oil flowrate (m ³ /s)
	V	= oil volume (m ³)
	t	= time (s)
	r	= spill radius (m)
	ν	= kinematic viscosity of oil (m ² /s)

Equating the driving force to each of the resistances yields the equations that define the two spreading regimes for oil on snow or ice:

	Continuous Source	Instantaneous Spill
Gravity-Inertia	$r = (gQ)^{1/4} t^{3/4}$	$r = 1.5 (gV)^{1/4} t^{1/2}$
Gravity-Viscous	$r = (gQ^2 / \pi \nu)^{1/2} t^{1/2}$	$r = (gV^2 / \pi \nu)^{1/2} t^{1/4}$

Figure 5 shows the continuous source data of McMinn and Golden (1972) and Glaeser and Vance (1971) plotted in non-dimensional format and the theoretical equations for the two spreading regimes. Although the data fit is not perfect, the trend certainly indicates that spreading of continuous oil releases on snow or ice occurs primarily in the gravity-viscous regime. Figure 6 shows the instantaneous release data of Glaeser and Vance (1971) for diesel and crude spilled on snow covered Arctic ice, the data of Kawamura et al. (1986) for the spread of bayol and pentanol on ice and the equation of Chen et al. (1974) based on numerous small scale oil on ice and snow spreading experiments. The fit of these various data to the theoretical equations for the two spreading regimes, though far from perfect, certainly indicates that initial spreading of instantaneous spills on snow or ice is governed by the gravity-inertia regime but, the spreading quickly reverts to the gravity-viscous regime.

In summary, the spreading of oil on snow or ice for a continuous source or instantaneous spill can be adequately modelled by the equations given for gravity-viscous spreading.

Infiltration of Oil into Snow

Again the literature review revealed several studies of oil infiltration into a snow pack (in fact one standard method for determining the permeability of a snow pack is to use kerosene to measure infiltration rates).

The flow of liquids through a permeable media is governed by the D'Arcy equation which can be written as:

FIGURE 5

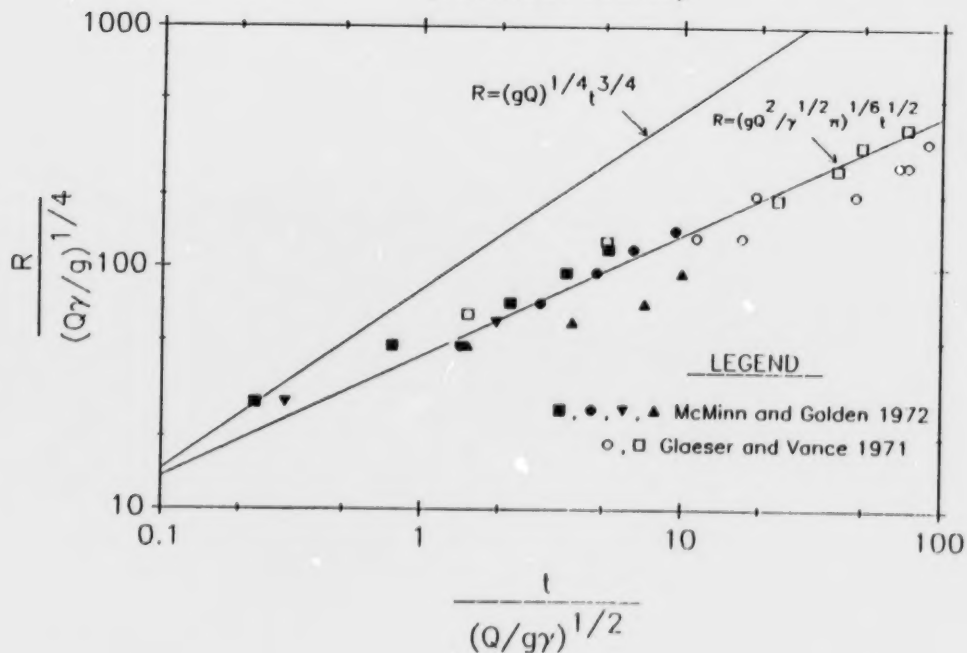
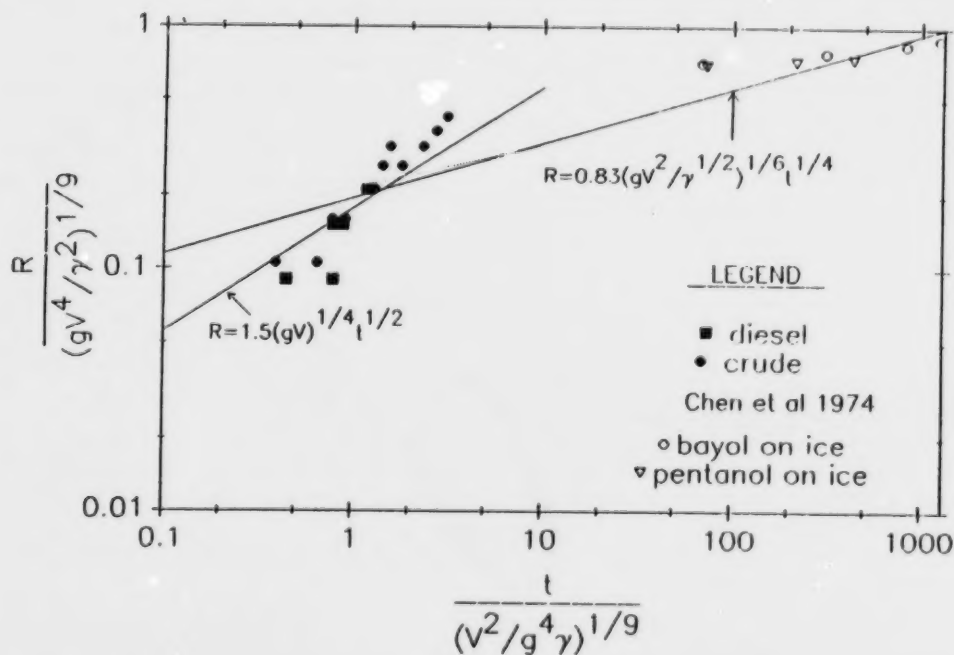
NON-DIMENSIONAL SPREADING ON SNOW OR ICE
(continous source)

FIGURE 6

NON-DIMENSIONAL SPREADING ON SNOW OR ICE



$$Q = KA\Delta P/\mu L$$

where

K	=	specific permeability of snow (m ²)
A	=	flow area (m ²)
L	=	flow path length (m)
ΔP	=	pressure driving force along flow path (Pa)
μ	=	dynamic viscosity of fluid (Pas)

Following the derivation of Mackay et al. (1974) for flow into snow beneath a surface spill:

for $\Delta P = \gamma_g (x+L)$ where x = thickness of oil on snow (m)

$$Q = KA\gamma_g (1+x/L)/\mu$$

and the linear rate of penetration of oil into snow is

$$dL/dt = (K\gamma_g/E\mu) (1+x/L)$$

where

E	=	void fraction of snow
	=	porosity
	=	$1 - \rho_s/\rho_i$
ρ_s	=	snow density (kg/m ³)
ρ_i	=	ice density
	=	917 kg/m ³

The major unknown in these equations is K, the specific permeability of snow which is a function of snow density, crystal size and age. A simple equation for specific permeability is presented in the next section.

Horizontal Flow of Oil in Snow

Theory The horizontal flow of oil in snow at an impermeable layer was modelled as follows, beginning with the D'Arcy equation rewritten as:

$$L = KA\Delta P/\mu Q$$

substituting

$$A = 2\pi Lh,$$

$$V = Qt,$$

$$h = V/E\pi L^2,$$

and

$$\Delta P = \gamma_g h = \gamma_g V/E\pi L^2$$

where h = height of oil layer in snow (m)

yields $L = (2K\gamma_g V/\pi E^2 \mu)^{1/4} t^{1/4}$ for an instantaneous spill, or

similarly

$$L = (2K\gamma_g Q/\pi E^2 \mu)^{1/4} t^{1/2}$$
 for a continuous release

Specific Permeability of Snow

Shimizu (1969) has shown that the specific permeability of snow may be adequately determined from

$$K = 7.7 \times 10^{-2} d_o^2 \exp(-7.8 \rho_s / \rho_i)$$

where d_o = mean grain size of snow (m)

For situations where snow properties are unknown, the permeability can be estimated to within a factor of 2 by using $d_o = 0.5$ mm and $\rho_s = 400$ kg/m³ to yield

$$K = 6 \times 10^{-10} \text{ m}^2$$

This is a reasonable approximation since K appears to the power 1/4 in the equation for horizontal flow in snow, and thus a margin of error in K of 200% translates to an error of less than 20% in L .

Mackay et al. (1974) experimentally determined K for snow with a variety of oils. Their results ranged from 1.5 to 7.8×10^{-10} m².

Experiments

Figure 7 shows the results of the mid-scale experiments of oil spreading under snowpack on ice expressed as radius vs time. The oil temperature was 7°C when it was spilled; the average flowrate during release was 1.4 L/s. The snow at the first test plot (Run 1) was 15 cm thick, had an average density of 173 kg/m³ and was comprised of crystals ranging in size up to 1 mm and averaging 0.5 mm. The artificially densified and thickened snow at the second test site was 18.5 cm thick, had a density of 272 kg/m³ (upper half = 296 kg/m³; lower half = 248 kg/m³) and was also comprised mainly of 0.5 mm size crystals. Air temperature during the spills was -8 to -10°C; the snow temperature at the ice was -3 to -3.5°C. Winds were light (1 m/s) during the duration of the tests.

Figure 8 shows the height of oiled snow remaining, after spreading ceased, across each test site. Except for the central area (with a diameter of some 2 m) the equilibrium height of oiled snow was constant at about 2-3 cm.

Figure 9 shows the fit of the data to the theoretical models. Although there is considerable scatter, the theory for spreading of an instantaneous release (i.e., equation with V) fits the data, after a time of 150 s (the oil release time), reasonably well. The theory for spreading of a continuous source, although it approximates the data in the time period up to 150 s, does not appear to have the correct slope. This may be due to the fact that the oil was warm (8°C) when poured and could have melted the snow as it spread until it cooled to below 0°C.

Figure 10 shows the fit of the experimental data to the instantaneous release model in a non-dimensional format. Also shown are the data from a 0.4 m³ experimental spill reported by Mackay et al. (1974). With the exception of the data collected during the discharge (up to a non-dimensional time of about 5000) the model fits the data reasonably well.

Evaporation of Oil In Snow

The trays containing the oil for evaporation studies were left outdoors for two weeks. A warm spell on the 14th day caused the snow to melt and end the experiments.

Figure 11 shows the oil and air temperatures recorded during the experiments as well as the calculated means for each tray. Figure 12 shows the measured wind

FIGURE 7
MID-SCALE
SPREADING UNDER SNOW

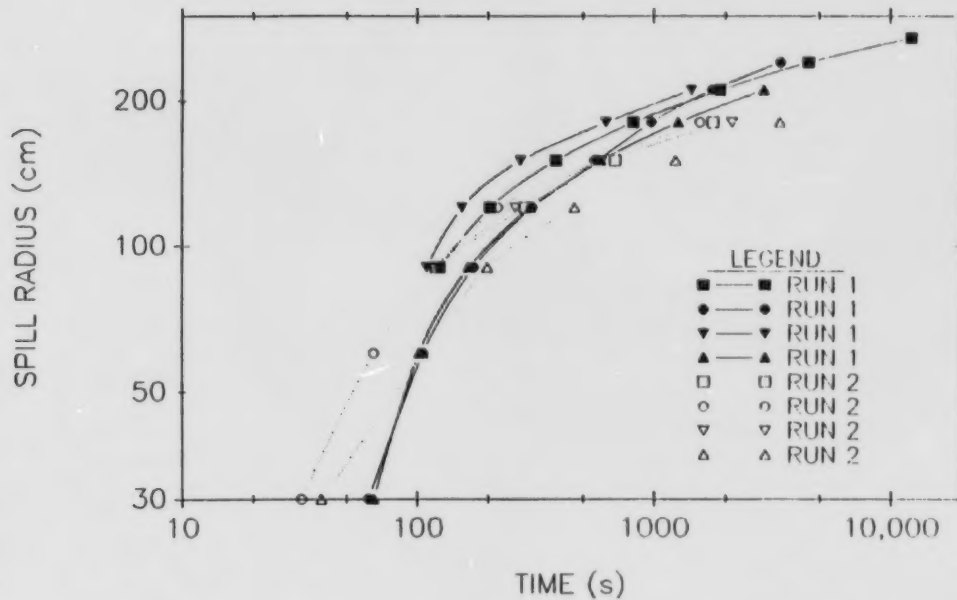
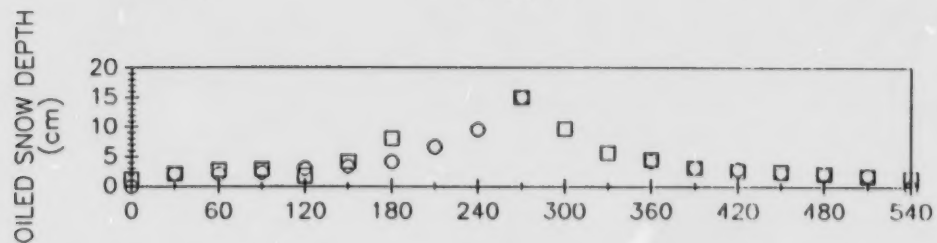
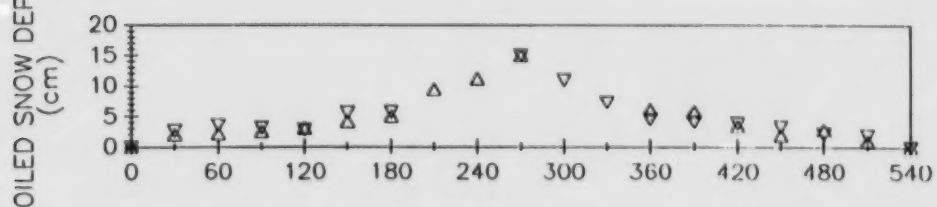


FIGURE 8
COMPARISON OF SPILL PROFILES

SPILL 1



SPILL 2



DISTANCE ACROSS SPILL (cm)

FIGURE 9
SPREADING UNDER SNOW - COMPARISON OF THEORY WITH DATA

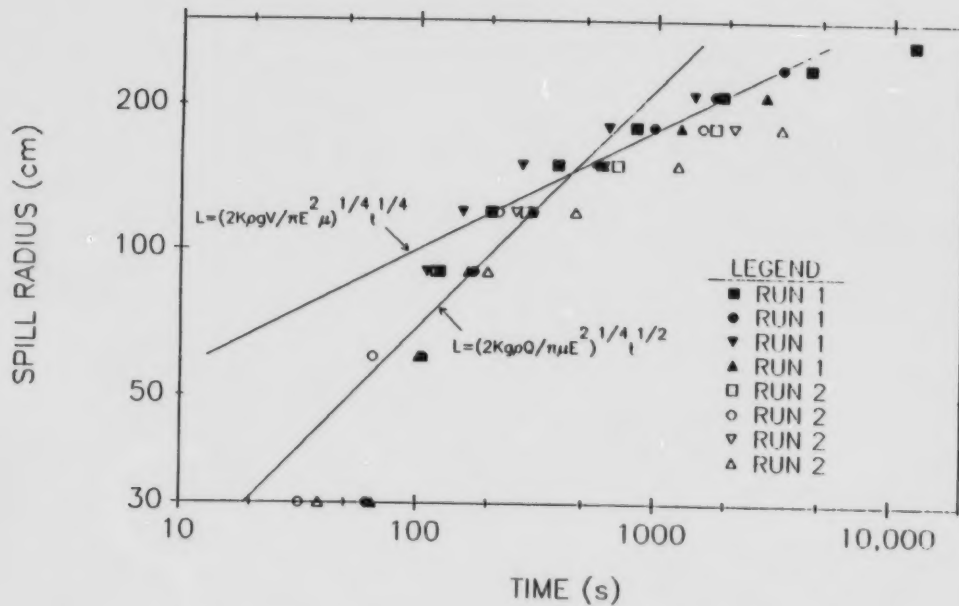


FIGURE 10
NON-DIMENSIONAL SPREADING UNDER SNOW

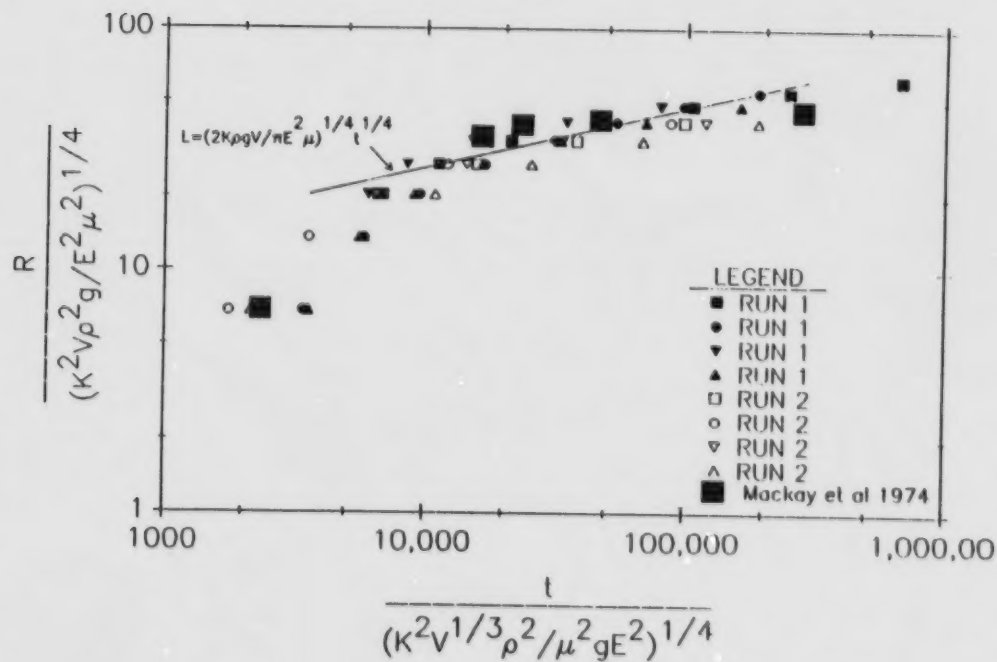


FIGURE 11
SMALL - SCALE EXPERIMENT TEMPERATURES

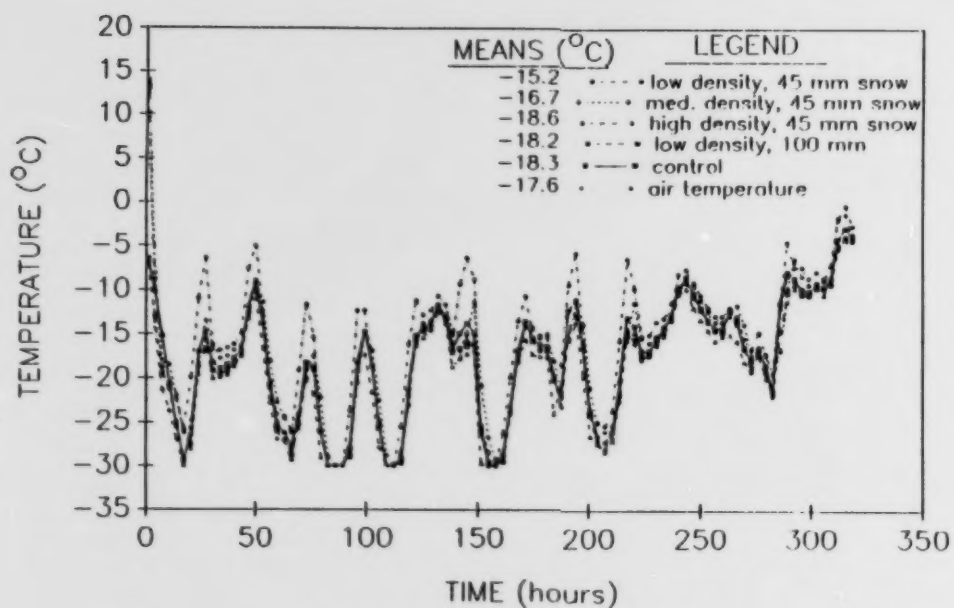
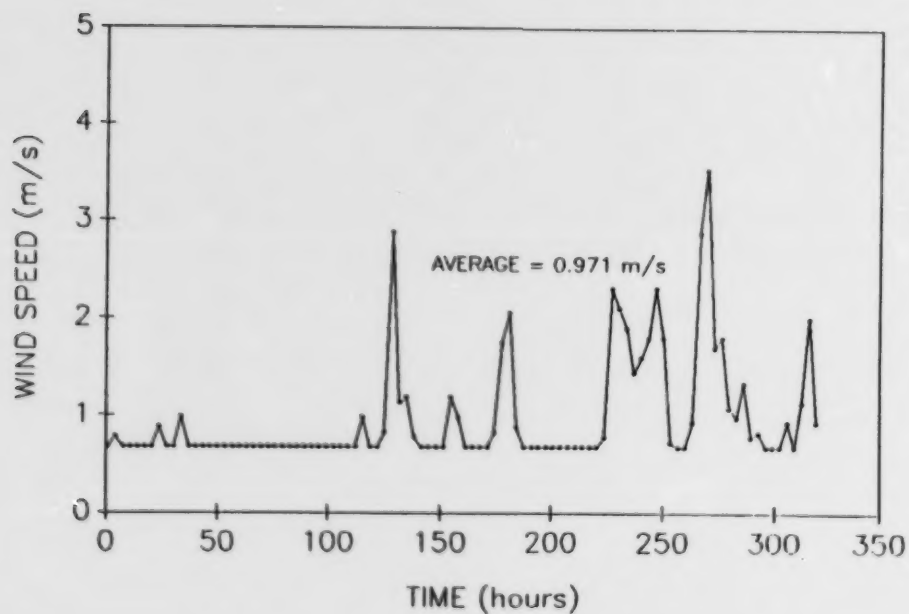


FIGURE 12
SMALL - SCALE EXPERIMENT WINDS



speeds at the test site. Since the lowest wind that activated the anemometer was 1.34 m/s, zero readings were arbitrarily assigned a value of 0.67 m/s.

Figure 13 shows the measured volume fraction evaporated for each of the trays as a function of time. Also shown are the data from the two mid-scale experiments. For the small-scale experiments, the control tray (no snow) experienced the greatest evaporative loss. Of the trays containing snow and oil, the one with 45 mm of uncompacted snow had the highest evaporative loss; increasing snow density and thickness reduced evaporation from the oil. At first glance the results from the mid-scale tests seem anomalous; however, it must be kept in mind that the temperature during the mid-scale tests (-3°C) was much higher than during the small-scale tests (-17°C), thus the mid-scale tests could be expected to experience more rapid evaporation. In addition, as will be discussed later, the temperature difference between the two test series spans the pour point of the fresh MSW oil (-8°C). As has been recently discovered (S.L. Ross and DMER 1987) oils at temperatures below their pour points (as is the case with the small-scale tests) evaporate much more slowly than expected due to the development of an internal resistance to mass transfer in the semi-solid oil.

Determination of the Snow Mass Transfer Coefficient Using the evaporative exposure approach of Stiver and Mackay (1982) where:

$$F_v = (T/10.3 T_G) \ln (1 + (10.3 T_G/T) \theta \exp (6.3 - 10.3 T_0/T))$$

$$\text{and } \theta = kAt/V = kt/x$$

where

F_v	=	volume fraction evaporated
T	=	environmental temperature ($^{\circ}\text{K}$)
T_G	=	slope of modified ASTM distillation curve ($^{\circ}\text{K}$)
	=	539 $^{\circ}$ K for MSW crude
T_0	=	intercept of modified ASTM distillation curve ($^{\circ}\text{K}$)
	=	385 $^{\circ}$ K for MSW crude
θ	=	evaporative exposure coefficient
k	=	mass transfer coefficient (m/s)
A	=	spill area (m^2)
V	=	spill volume (m^3)
x	=	slick thickness (m)
t	=	time (s)

$$\text{setting } A = (T/10.3 T_G)$$

$$\text{and } B = (10.3 T_G/T) \exp (6.3 - 10.3 T_0/T)$$

$$\text{gives } F_v = A \ln (1 + B\theta)$$

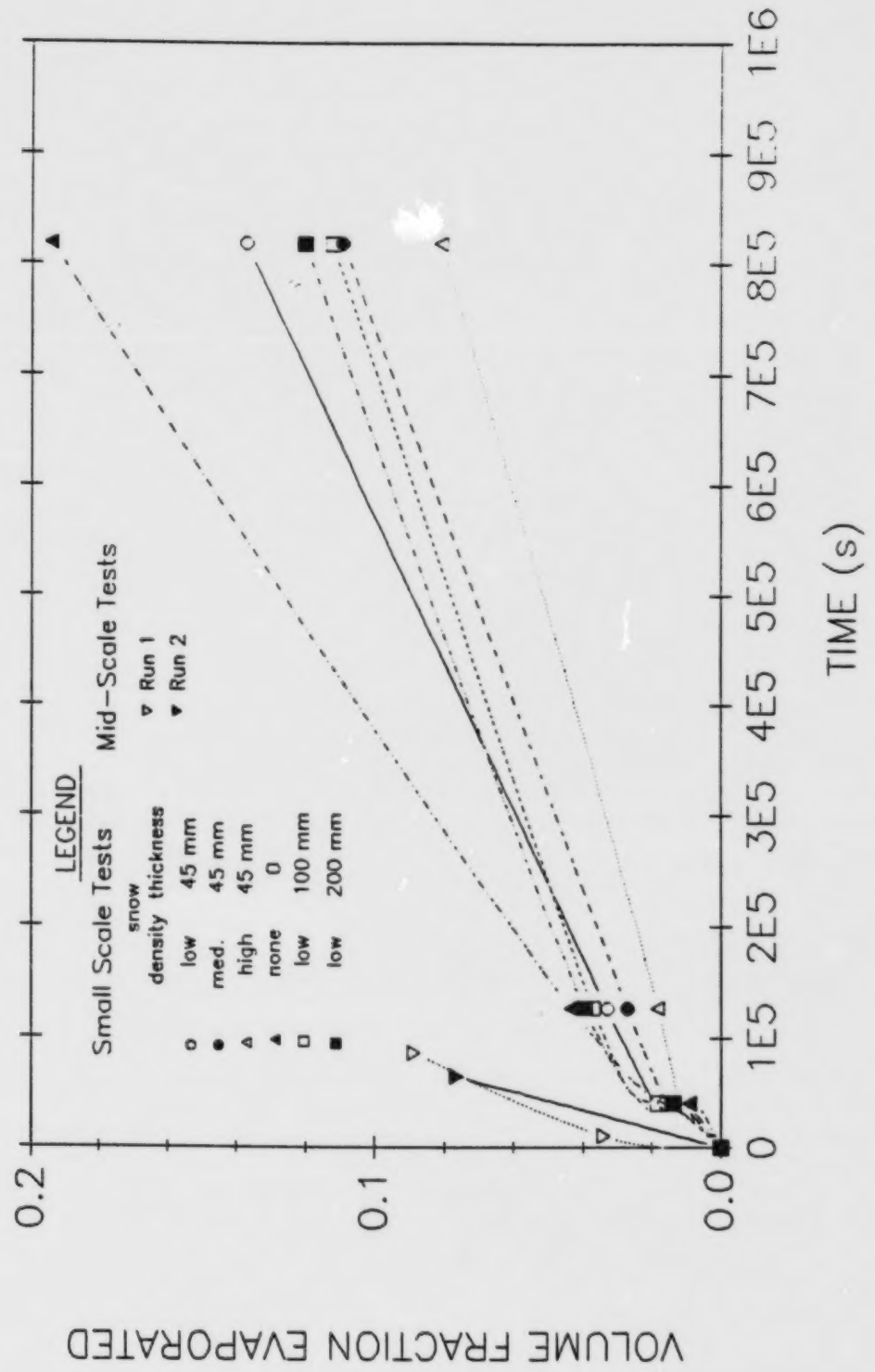
rearranging yields

$$\theta = (\exp (F_v/A) - 1)/B$$

or substituting for θ

$$x (\exp (F_v/A) - 1)/B = kt$$

FIGURE 13
EXPERIMENTAL EVAPORATION RESULTS



thus a plot of $x(\exp(F_v/A)-1)/B$ vs t will have a slope of k , the overall mass transfer coefficient. Figure 14 shows such a plot.

Using the resistance-in-series approach to mass transfer:

$$1/k = 1/k_w + H/k_o + L/D_s$$

where k_w = air-side mass transfer coefficient (m/s)
 $= 0.002U^{0.78}$ (Mackay and Matsugu 1973)
 k_o = oil internal mass transfer coefficient (m/s)
 H = Henry's law constant for the oil
 D_s = diffusivity of oil vapours in snow (m^2/s)
 L = depth of oil below snow surface (m)

thus a plot of $1/k$ (the slope of the curves in Figure 14) against snow depth (L) should have a slope of $1/D_s$ and intercept of $1/k_w + H/k_o$. Such a plot is given in Figure 15. The least squares fit to the small-scale data from the trays with uncompacted snow gives a slope of 5.5×10^4 s/ m^2 or $D_s = 1.8 \times 10^{-5} m^2/s$. This is close to reported values of water vapour diffusivities in snow of $6 \times 10^{-5} m^2/s$ (de Quervain 1972). A line drawn from 500 on the y-axis (equivalent to $1/k_w$ for the mid-scale tests, conducted at temperatures above the pour point), through the two mid-scale data point would have a slope very close 5.5×10^4 .

The intercept is 6.4×10^3 equivalent to $(1/k_w + H/k_o)$. With $k_w = 2 \times 10^{-3}$ and H for fresh MSW = 3.5×10^{-5} the internal resistance to mass transfer (k_o) equals 6×10^{-9} m/s. This value is quite close to that determined for waxy oils at temperatures below their pour point (5×10^{-9} m/s).

Although there are insufficient data points to accurately determine the effects of snow density on the diffusivity of the snow, Figure 16 shows the relationship between D_s and the specific gravity of the snow. The values of D_s for the medium and higher density small-scale experiments come from the slope of the line drawn from the control data point (snow depth = 0) to the respective density data point. These data indicate that diffusivity varies inversely with the fourth power of snow specific gravity. Although it makes sense that diffusivity should decrease with increasing snow density, a dependence on the fourth power of density seems excessive. With the present data it is not possible to determine more accurately the true relationship; more experiments are required.

Oil Transport by Blowing Snow

As noted previously, at the time of writing these experiments were still ongoing. As such, no data is yet available.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

1. Oil spreading on snow or ice can be modelled using the equations for the gravity-viscous spreading regime:

For a continuous source

$$r = (g Q^2 / \pi \gamma)^{1/2} t^{1/6} t^{1/2}$$

FIGURE 14
Determination of Overall Mass Transfer Coefficient

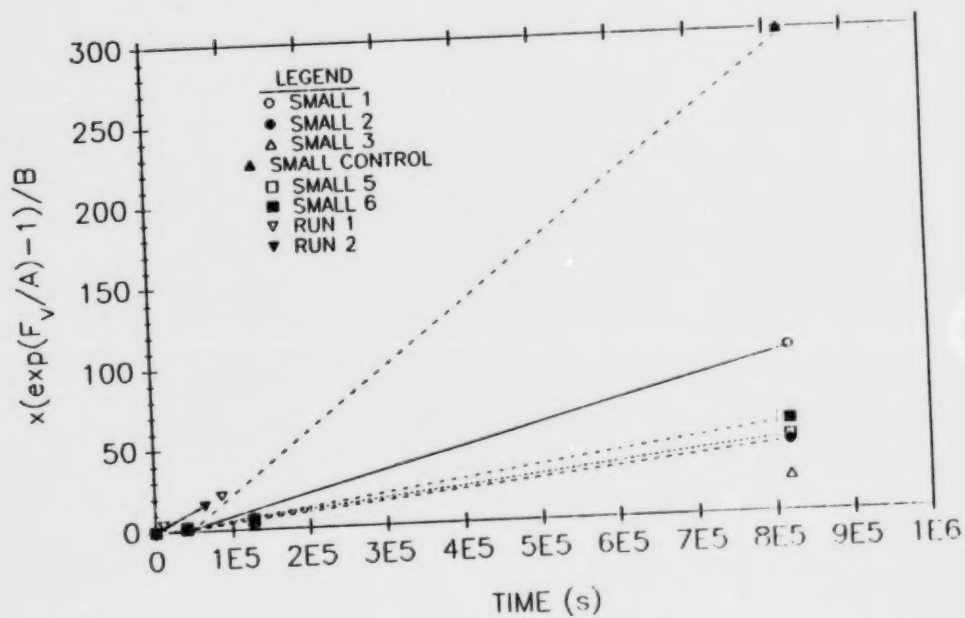


FIGURE 15
DETERMINATION OF DIFFUSIVITY IN SNOW

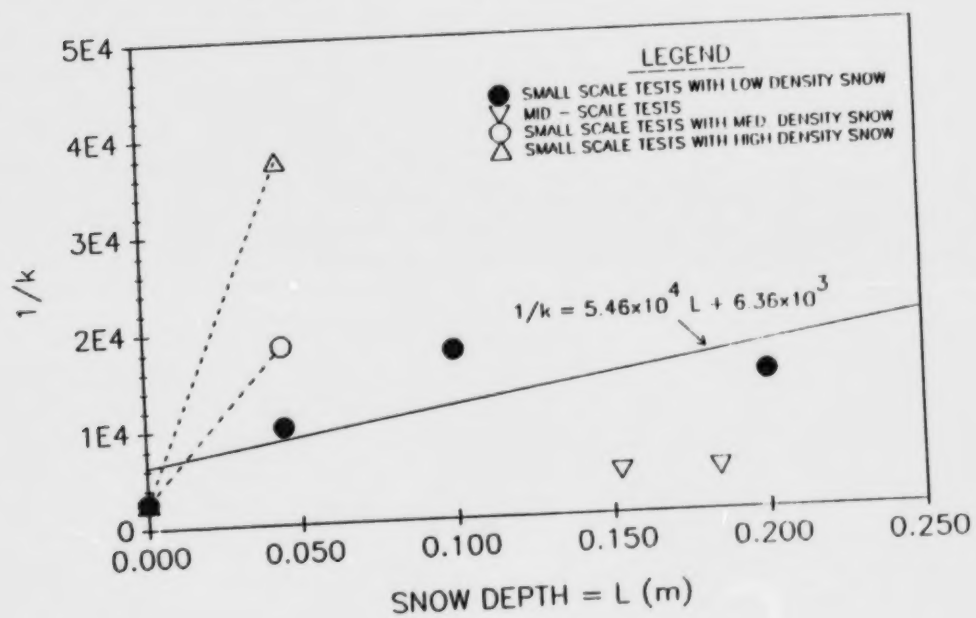
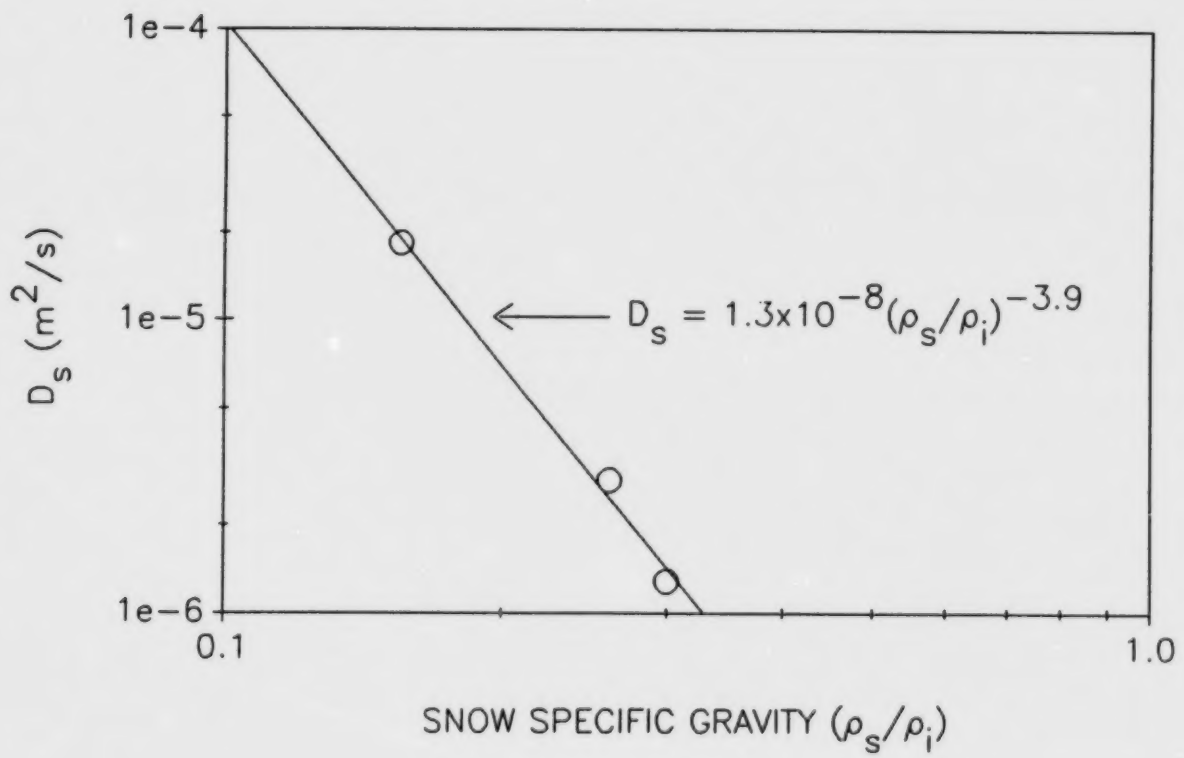


FIGURE 16
VARIATION IN D_s WITH SNOW DENSITY



and for an instantaneous spill

$$r = (gV^2/\pi \nu^{1/2})^{1/6} t^{1/4}$$

2. Oil infiltration into a snowpack can be modelled using the D'Arcy equation:

$$Q = KA \gamma_g (1 + x/L) / \mu$$

and

$$dL/dt = (K \gamma_g / E\mu)(1 + x/L)$$

3. The horizontal spreading of oil on an impermeable surface beneath a snowpack can be modelled by:

For a continuous source

$$L = (2Kg \gamma_g Q / \pi E^2 \mu)^{1/4} t^{1/2}$$

and for an instantaneous release

$$L = (2Kg \gamma_g V / \pi E^2 \mu)^{1/4} t^{1/4}$$

in which

$$K = 7.7 \times 10^{-2} d_o^2 \exp(-7.8 \gamma_s / \gamma_i)$$

4. The evaporation of oil beneath a snowpack can be modelled by the evaporative exposure approach using:

$$1/k = 1/k_w + H/k_o + L/D_s$$

where the diffusivity in snow was found to be

$$D_s = 1.3 \times 10^{-8} (\gamma_s / \gamma_i)^{-3.9}$$

Recommendations

Further work on the effect of snow density on oil evaporative flux should be conducted.

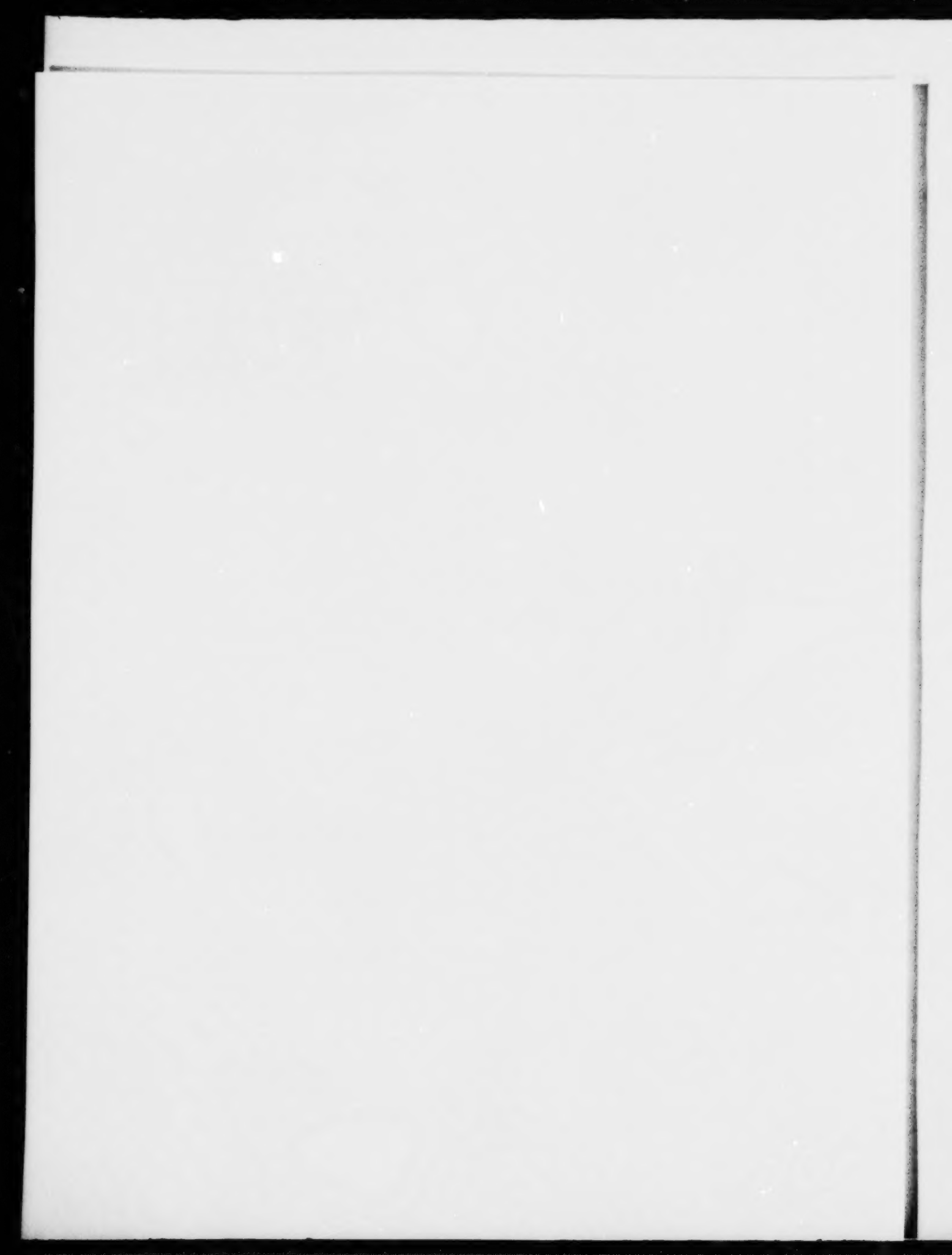
ACKNOWLEDGEMENTS

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AN INVESTIGATION OF BUBBLE GROUPS FROM AN UNDERSEA OILWELL BLOWOUT

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ABSTRACT

The leading edge of the starting bubble plume from a subsea oilwell blowout resembles a single-phase thermal in appearance, and the mechanism of gas release from the wellhead after a blowout is also conducive to the production of thermal-like structures, resulting in intermittent plume behaviour. Therefore, the authors believe it may be more appropriate to model blowout plumes as a series of bubble groups or "thermals" rather than as a continuous plume. A laboratory investigation of individual bubble group behaviour has been undertaken as the starting point for the development of such a model. This paper discusses some of the progress made in this investigation. Based on the experimental results to date, the "thermal" model assumption appears to be justified.

INTRODUCTION

A major impediment to the full exploration and exploitation of oil and gas reserves in Arctic waters has been the concern about the possible damage from an uncontrolled subsea blowout. Should a blowout occur, the buoyancy of the gas will cause hydrocarbons and entrained seawater to rise to the ocean surface in a structure which is commonly called a bubble plume. At the surface, the vertical motion deflects radially outwards from the plume with little loss in momentum. A shallow, fast-moving layer is generated which transports the oil in the plume a considerable distance from the blowout point. The large area and small thickness of the slick make containment and collection more difficult than in the case of an equivalent surface spill.

Underwater blowouts are most likely to occur during exploration drilling when the blowout preventer is mounted at the wellhead rather than on top of the riser, as is usual in the production phase. A common misconception is that a floating drilling vessel will sink if a blowout occurs beneath it, because the gas bubbles will "aerate" the water and the vessel will lose its buoyant support. Although this belief has been disproved by recent technical studies [1], an accurate method of predicting the hydrodynamic structure is still necessary to calculate the forces generated by the plume on drillships or floating platforms at the surface above the wellhead. Milgram and Erb [1] have made an attempt to estimate the effect of a bubble plume on semi-submersibles and other vessels, but only after a steady-flow regime has been established. To date, the initial impact of a plume on such a structure has never been studied.

Large-scale investigations into the behaviour of blowout plumes have shown that the starting plume structure is like a single-phase thermal in appearance [2]. The mechanism of gas release from the wellhead is also conducive to the production of thermal-like structures. As the gas emerges, a large bubble forms with either a rounded or fluted shape. As the bubble releases from the orifice, it shatters into smaller bubbles [3]. This

phenomenon would tend to explain the frequently observed unsteady nature of a bubble plume, which can lead to fluctuating dynamic forces on a drilling vessel. If fluctuations occur at a frequency which excites a dynamic response in the rig, oscillations may result which are likely to be larger than those from steady-flow predictions. A plume model based on the intermittent release of bubble "thermals" rather than on the assumption of steady flow has been proposed by the authors as an appropriate solution to both of these problems.

A laboratory investigation of individual bubble group behaviour has been undertaken as the starting point for the development of such a model. This paper discusses some of the progress made in this investigation, which is also a Ph.D. research topic.

BACKGROUND

The term "thermal" has gained acceptance in meteorological literature to denote the turbulent motion arising from a suddenly released source of buoyancy. The buoyancy of atmospheric thermals is due to a density difference between the thermal and the surrounding air, resulting from a difference in temperatures. The lighter fluid parcel rises vertically, entraining the surrounding air as it progresses by convective mixing across the density interface. Using dimensional arguments, a similarity solution can be formulated for single-phase thermals based on powers of the height above a point source and the total buoyancy released. The velocity of the thermal front is proportional to the square root of the buoyancy divided by the height, while the radius is linearly related to the height by a proportionality constant which is usually termed the entrainment coefficient α . This type of a solution is possible for a thermal because it exhibits a similar interior circulation pattern throughout its lifetime.

Groups of bubbles suddenly released into quiescent fluid take on a configuration similar to that observed in single-phase thermals [4] both in shape and growth pattern. However, the presence of a large local density difference between the two immiscible phases in a rising bubble group implies that its behaviour could differ from that of a single-phase thermal, where the density variations are usually small. This has been found to be the case by Krishnappan [5] in his detailed study of solid-particle clouds dispersing in water; the only other two-phase thermal investigation known to the authors.

Research into the behaviour of air-bubble plumes has demonstrated notable similarities and differences between two-phase and single-phase plumes, which are normally modelled using the same type of similarity argument used to describe thermal behaviour. The differences are largely due to the high density ratio between the dispersed and continuous phases and the uneven distribution of buoyancy within the plume structure. As air is so much lighter than water ($\rho_g/\rho_g \approx 800$), the gas bubbles tend to move faster than the surrounding liquid whether it is in motion or not. The differential, or slip, velocity between the rising air bubbles and water plume flow results in smaller plume velocities, thus reducing the vertical transport relative to that associated with a single-phase plume having the same buoyancy. On the other hand, the compressibility of air causes the buoyancy to increase with height, as the gas bubbles expand due to decreasing hydrostatic pressure as they ascend.

Enough similarities exist, however, so that it is possible to model two-phase plumes in the same manner as miscible plumes, as long as the slip velocity between the two phases, the dispersion ratio λ and the momentum

amplification γ due to the presence of the gas phase are taken into account [6]. One would think, therefore, that it should be possible to model a bubble group as a single-phase thermal by including these parameters in the equations.

DIMENSIONAL ANALYSIS

The variation of the dependent parameters α , λ and γ , which control the global behaviour of a bubble plume is most easily expressed in terms of dimensionless groups. Rowe and Poon [6] showed that in round bubble plumes these parameters seem to depend solely on a dimensionless number which they called the bubble plume Weber number:

$$Bu_r = \sqrt{\frac{\rho_l (Q_{gA}^4 g^3)^{1/5}}{\sigma}} \quad (1)$$

If the appropriate length and velocity scales for round bubble plumes [7]:

$$L_r = (Q_{gA}^2 / g)^{1/5} \quad (2)$$

$$U_r = (Q_{gA}^2 g)^{1/5} \quad (3)$$

are substituted into Bu , it may be simplified further as:

$$Bu = \sqrt{\frac{\rho_l L}{\sigma}} U \quad (4)$$

The above scales are the same as the characteristic scales encountered in single-phase plume studies.

Laureshen and Rowe [8] demonstrated a dependence on the bubble plume Weber number for plane bubble plumes, as long as the appropriate length and velocity scales for plane plumes were substituted in the simplified form of Bu :

$$L_p = (Q_{gA}^2 / g)^{1/3} \quad (5)$$

$$U_p = (Q_{gA} g)^{1/3} \quad (6)$$

A similar analysis was performed to see if the anticipated dependent parameters for bubble thermals could also be expressed as functions of the bubble plume Weber number. The appropriate length and velocity scales for bubble thermals have been calculated as:

$$L_t = V_A^{1/3} \quad (7)$$

$$U_t = (V_A^{1/3} g)^{1/2} \quad (8)$$

which implies that the appropriate form of the bubble plume Weber number for bubble thermals should be:

$$Bu_t = \sqrt{\frac{\rho_l V_A^{2/3} g}{\sigma}} \quad (9)$$

It can be shown, using dimensional analysis, that the bubble thermal parameters can be expressed as a function of three dimensionless groups:

$$\frac{\alpha}{\lambda} = f \left[\frac{v_A^{1/3}}{\frac{\Delta \rho H_T}{\rho_L}}, \frac{\rho_L (v_A g)^{1/2}}{\mu}, \frac{\rho_L v_A^{2/3} g}{\sigma} \right] \quad (10)$$

The first of these can be recognized as a form of densimetric Froude number, the second as a liquid Reynolds number and the third as a Weber number. Taking the square root of the third dimensionless group gives the bubble plume Weber number predicted for bubble thermals.

Although the Reynolds number Re is a useful parameter in determining the transition to turbulence, once a flow has become turbulent this dimensionless group is of little importance as far as the large-scale motion is concerned [9]. The flow in bubble thermals should always be turbulent due to the shear generated by the bubble wakes. Thus, the global behaviour of bubble groups should be relatively insensitive to the Reynolds number, although Re will still determine the small-scale energy dissipation level. For this reason, it is anticipated that molecular viscosity will not be a significant variable in the bubble thermal experiments.

Examination of the remaining dimensionless groups shows that the variables which could affect the behaviour of bubble thermals are the injected volume, the height of the water above the orifice, surface tension and gravitational acceleration. Since the force of gravity is a constant, the other three parameters were chosen as the dependent variables in the laboratory work.

BUBBLE THERMAL EXPERIMENTS

While a number of analytical and experimental investigations of bubble plumes appear in the literature [10], all of the published data is for air-water systems. In order to provide a basis for comparison between bubble thermals and bubble plumes, it was decided to use water as the continuous phase and air as the dispersed phase in the current work.

The bubble thermal experiments were carried out in two tanks. The smaller tank (0.27 x 0.27 x 0.79 m) was constructed of aluminum with glass viewing windows on three sides. Its size was dictated by the optical limitations of the single-component laser-Doppler anemometer (LDA) which was used to verify liquid velocities. The large tank (1.13 x 1.13 x 1.22 m) had plexiglass walls on all sides, and was built to ensure that wall proximity did not affect the small tank results.

The same air-injection apparatus was used for both tanks. Air was supplied through a 207 kPa regulator to a calibrated volume with an electric solenoid valve at one end and a mercury manometer at the other. A time delay switch opened the solenoid and released air to a sintered steel airstone mounted at the tank base. The volume of air injected was calculated using the pressure change in the calibrated volume. Use of the airstone ensured uniformly sized bubbles ranging in diameter from two to eight millimetres.

Still and video cameras were used to record the flow dynamics of the gas and liquid phases. A high-speed camera (16 mm Hycam) was used to examine flows close to the bubbler (airstone), where velocities were highest. Fluorescein dye was used to visualize the fluid motion. Measurements of group size and position as a function of time and height were made from the

resulting photographs. The time between successive exposures was calculated using timing marks on the Hycam, the built-in clock on the video system and by incorporating a clock with a 0.01 second resolution in the still photographs.

EXPERIMENTAL OBSERVATIONS

The experiments demonstrate that two-phase bubble groups do not exhibit the group circulation and constant overall entrainment of the surrounding fluid characteristic of conventional thermals. Two figures have been included which show the results from five runs with the same injected air volume at the same water height in the small tank. Figure 1, which is a plot of the radius of the thermal's widest point versus height above the top of the airstone, illustrates the two stages of growth which were identified for each bubble group. The first stage, which typically extends 10-15 cm above the bubbler, is characterized by large entrainment and accelerating velocity near the injector. All of the bubble groups, regardless of injected volume and water height, had an entrainment coefficient α of approximately 0.2 in this initial growth period. This is comparable to single-phase values, which range from 0.1 to 0.35, with an average of about 0.25 [11]. High-speed photographs confirmed that the bubbles circulate with the fluid in the region nearest to the bubbler, so the large value of α for this growth stage is not surprising.

In its second stage of growth, the bubble thermal radius also grows linearly with height. However, the value of α for this stage is an order of magnitude smaller than that for the initial growth period. The entrainment coefficients were constant for each injected volume and ranged from 0.06 to 0.08. They were of the same order of magnitude as entrainment coefficients for bubble plumes. The thermal velocity decelerated at the beginning of this region down to a value approaching the terminal velocity of an individual bubble (0.2 - 0.25 m/s). It then increased again with height due to the increased buoyancy of the bubbles from decreasing hydrostatic pressure. Figure 2 illustrates the velocity pattern in a typical bubble thermal.

The transition between the two growth stages was characterized by the release of a vortex ring from the main body of the thermal. The vortex remains at the top of the moving fluid in the wake of the bubbles, and as it rises it expands linearly and decelerates. On the average, the vertical velocity of the bubble group is two to three times that of the vortex. The water in the wake of the bubble group continues to rise even after the bubbles have passed above the free surface.

If bubble groups are released sequentially, with a time delay between each injection, the rearward groups will rise at a faster velocity than the preceding ones and amalgamate to form a plume-like structure.

DISCUSSION

The experimental evidence to date shows that the entrainment coefficient for a bubble thermal in its second stage of growth is proportional to injected air volume and is independent of water depth. Decreasing the surface tension of the water also increases the entrainment coefficient for a given injected volume, chiefly through the mechanism of reducing the bubble diameter. This reduces the slip velocity, enabling the thermal to more closely approximate single-phase thermal behaviour. Because of this evidence, the prediction that global bubble thermal behaviour should depend only on the Weber number, and not the Froude number, appears to be correct.

FIGURE 1 - RADIUS CHANGE WITH HEIGHT

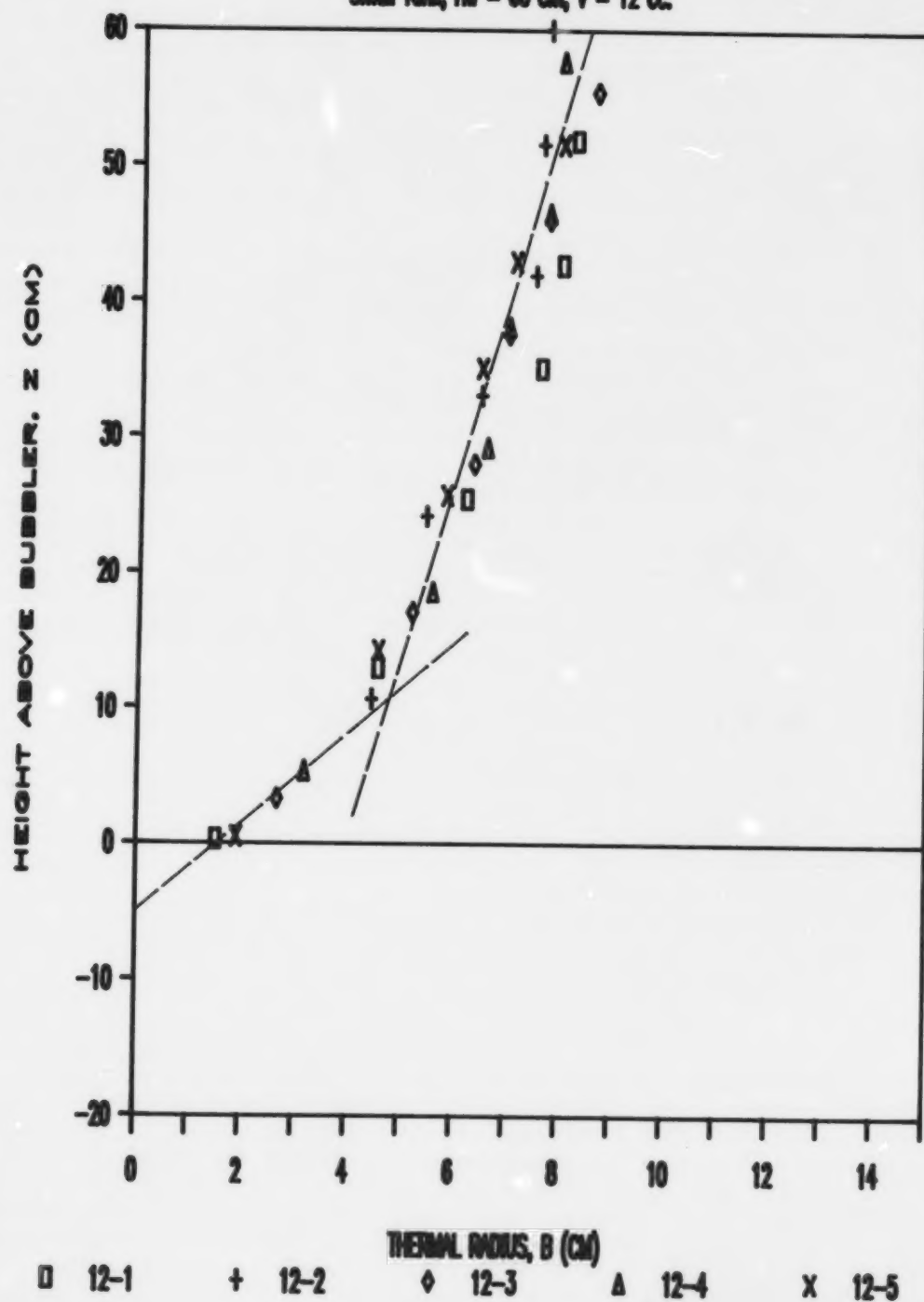
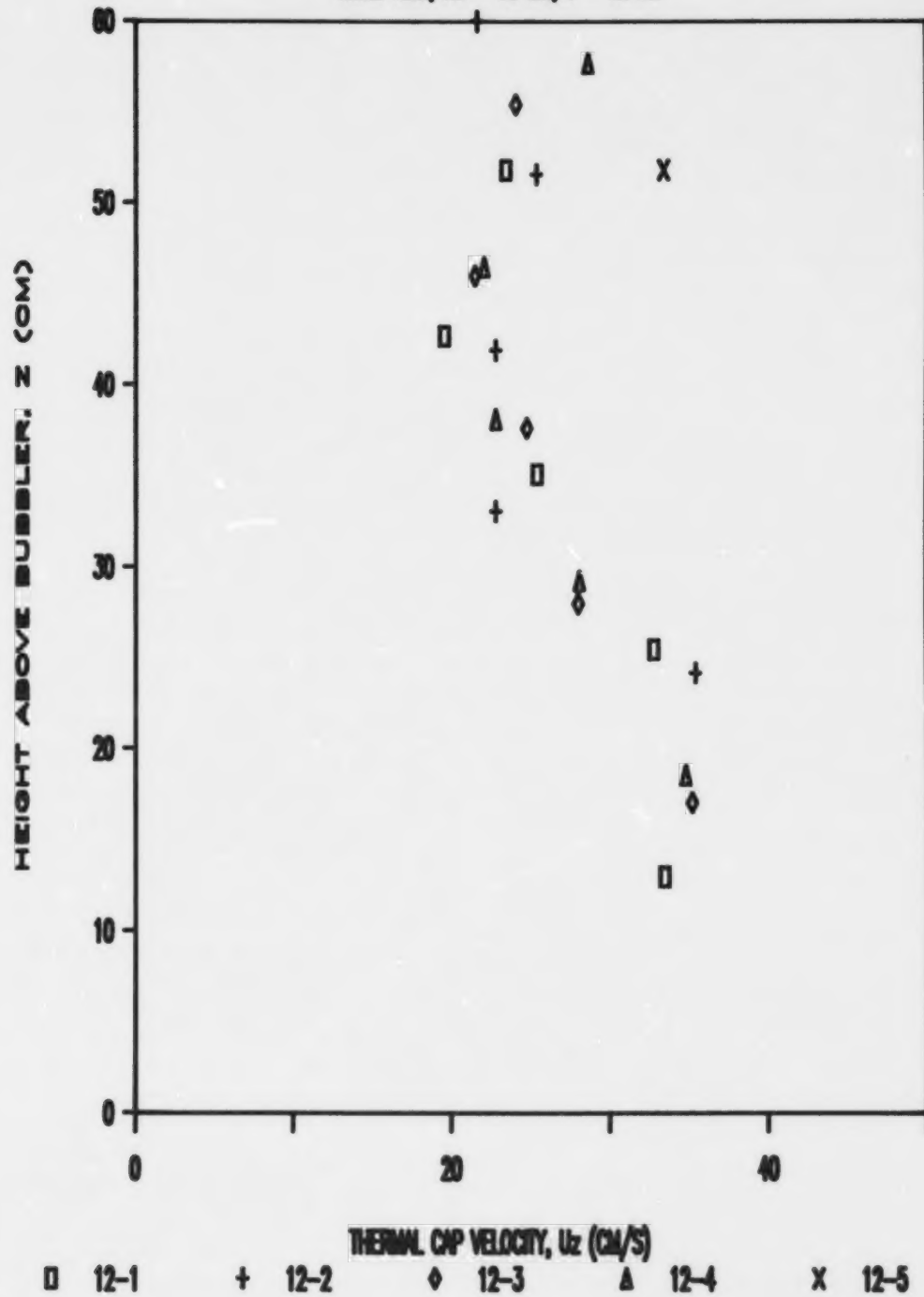
Small Tank, $H_w = 80$ cm, $V = 12$ cc.

FIGURE 2 - VELOCITY CHANGE WITH HEIGHT

Small Tank, $H_0 = 60$ cm, $V = 12$ cc.



Although the bubble groups retained the shape of single-phase thermals after the transition point, no group circulation was exhibited by the bubbles in the second growth stage. This implies that conventional thermal equations should be inadequate to model a bubble thermal in this stage, since the entrainment assumption used to formulate thermal dynamics requires the same kind of turbulence structure and balance of forces at each height. Because the liquid in the bubble group wake appears to exhibit the type of circulation required to apply such a model, however, correlating the bubble motion to the liquid motion through the bubble slip velocity could be the answer to this problem.

Releasing bubble groups sequentially with a time delay between each air injection results in a structure which looks quite similar to a steady-state bubble plume. Thus, the assumption that bubble plumes can be modelled as a superposition of bubble thermal models appears to be justified, based on the laboratory results to date.

ACKNOWLEDGEMENTS

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NOMENCLATURE

B	bubble thermal radius at the widest point
Bu	bubble plume Weber number
g	gravitational acceleration
H_T	absolute source pressure head
L	length scale
Q_{gA}	volumetric gas flow rate at atmospheric conditions
Re	Reynolds number
U	velocity scale
U_v	vertical bubble thermal cap velocity
V_A^z	injected gas volume at atmospheric conditions
z	vertical coordinate
α	entrainment coefficient
γ	momentum amplification factor
λ	dispersion ratio
ρ_l	density of liquid phase
$\Delta\rho$	density difference between gas and liquid phases
σ	surface tension



Burning, Smoke Production, and Smoke Dispersion from Oil Spill Combustion

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ABSTRACT

The combustion of crude oil layers floated on water were studied to assess the potential of using combustion to mitigate oil spill. Burning rates for n-decane, toluene and Alberta Sweet crude oil were measured in a 1.2 m diameter pool. These were used to estimate the energy transfer rate required to vaporize the fuel as part of an energy balance at the liquid surface. Smoke emission per unit of fuel consumed was dramatically reduced in the case for burning oil layers thin enough to cause boiling in the supporting water layer. A new aging/dilution facility is described that allows for measurement of optical properties and sedimentation velocities as the smoke ages. These characteristics are important in estimating smoke properties downwind of the oil spill fire. A formulation is presented that will provide for estimates of oil spill fire smoke downwind particulate deposition for steady state burning and wind conditions, no stratification, and a known injection altitude.

BACKGROUND

In 1985, the Center for Fire Research (CFR) at the U.S. National Bureau of Standards (NBS) began studies of oil spill combustion under support from the Minerals Management Service (MMS) of the U.S. Department of the Interior. This work seeks to quantify the processes involved in oil spill combustion on open waters and in water filled channels formed in broken ice including measurements of smoke production and prediction of smoke dispersal. Additional technical support from Environment Canada has allowed the study to be broadened to include in the scope chemical analysis of the oil, oil residue, and oil smoke.

The long range goal of the research program is to provide measurements and means to make quantitative predictions of (a) the fraction of oil in a spill that can be consumed by an in-situ combustion process, (b) the characteristics of the residual oil, and (c) the characteristics of the combustion product flow from the burning oil. It is hoped that this information may be cast into a form that is usable by local officials and oil spill response professionals as part of the decision making process in the event of an oil spill.

Last year's study was the first part of a two part study to quantify (a) the thermal properties and burning characteristics of the crude oil, (b) the physical and chemical properties of the smoke generated in the combustion process, and (c) the expected dispersal of the soot through the atmosphere and deposition down wind of the oil fires. These included results

from experiments to quantify the burning of 0.60 m and 1.2 m diameter oil pool fires. Measurements of thermal radiation emission, smoke production and the polyaromatic hydrocarbon content of both the oil and the smoke were reported [1]. Initial calculations were presented to estimate the dispersal of smoke in the atmosphere characterized by a uniform wind velocity.

This year's effort emphasizes understanding of the crude oil vaporization process by burning both crude oil and selected pure hydrocarbons fuels in the 1.2 m diameter pool fire test facility. Soot production and chemistry during the rapid combustion period associated with boiling of the supporting water layer were measured to complement similar measurements collected prior to this boiling phase last year. Analysis of smoke dispersal in the atmosphere were continued by formulating a model for smoke particle settling time which is directly related to soot deposition on the ground remote from the combustion site.

BURNING CHARACTERISTICS

Previous experiments [1] were conducted to measure the burning characteristics of three types of crude oil floated on a water layer in a 1.2 m diameter pan. The principal emphasis was placed on measuring the flame-plume temperature, energy release rate, and radiation feedback to the oil surface over a range of thickness of the oil layer. Also measured and reported were amount of oil residue remaining and the transient and steady-state burning patterns including the nature of the vigorous burning phase involving boiling of the water sublayer. For Alberta Sweet, LaRosa, and Murban crude oils, it was found that an initial oil layer thickness of 10 mm was sufficient to establish a period of quasi-steady state burning leading subsequently to a characteristic vigorous burning period just prior to flame extinction.

In this part of the study, the principal emphasis is on a better understanding of the heat balance at the burning oil surface in order to develop an appropriate model of the burning and extinction processes. The experimental arrangement and instrumentation were essentially identical to that previously described. Most measurements were made using a 10 mm thick layer of Alberta Sweet crude oil floated on water, with the major variables being the initial water temperature and the effect of wind. In addition, tests were conducted with 10 mm thick layers of the pure hydrocarbons n-decane and toluene, which were intended to represent the paraffinic and the aromatic components respectively in crude oil. More detailed measurements and analysis was made of the regression (i.e. burning) rate of the oil, the radiation feedback, and the extent of heat conduction into the oil and water layers during the burning periods. This analysis provides a background for predicting conditions under which a burning crude oil layer on water will self-extinguish prior to complete fuel consumption.

Burning Experiments

A summary of the principal data recorded in this test series is given in Table 1. Certain features of the test setup and results are of particular interest:

The regression rate of the burning oil was determined by measuring the rate at which water was supplied to the 1.2 m diameter test pan in order to

maintain the oil surface exactly 12 mm below the top of the pan rim. The level control device is shown schematically in Figure 1. A sensitive diaphragm-type pressure transducer (No.1) is connected to a pressure tap near the bottom of the test pan. When a slight decrease in pressure corresponding to the burning of oil is noted, the operator manually adjusts valve No.2 to

Table 1 Summary of Measured Burning Data in 1.2 m Diameter Pan

Test	Oil Layer Thick	Wt	Max Flame Temp	Max RHR	Maximum Radiation Feedback ctr rim		Maximum External Radiation	Burning Rate	Burn Time	Initial Water Temp	Oil Residue
	mm	kg	°C	MW	kW/m ²		kW/m ²	mm/min	min	°C	kg
A05	10	9.36	900	2.16	52.7	38.6	11.3	2.4	4.00	10	1.10
A06	10	9.36	896	2.27	75.8	22.4	12.8	2.3	4.33	15	1.01
A07	10	9.36	880	1.61	81.5	21.4	9.2	2.2	4.47	28	1.32
A08	10	9.36	891	1.60	73.7	27.5	9.8	2.0	5.30	5	0.92
T01	5	5.00	848	1.52	22.9	14.4	9.2	2.4	2.2	8	0.14
T02	10	9.76	891	1.76	31.7	13.8	10.3	3.2	3.2	15	0.10
A09 ^a	5	4.68	287	1.37	48.4	19.2	19.3	4.0	1.77	16	0.86
A10 ^a	10	9.36	394	2.17	45.3	21.9	20.8	4.0	2.57	18	1.03
A11 ^b	10	9.36	465	1.95	42.3	16.0	20.9	2.9	3.0	20	1.18
D01	10	8.20	963	2.30	54.4	31.3	12.0	4.5	4.0	2	0.06
A12	10	9.36	890	2.48	65.6	21.5	11.9	1.6-4.8 ^c	3.60	5	0.84
T03	10	9.76	870	1.67	22.7	20.9	11.3	3.7	3.2	6	0.08
A13	10	9.36	893	2.56	60.5	26.2	12.3	1.7-4.8 ^c	3.9	10	0.92

^a Applied wind velocity 2.5 m/s

^b Applied wind velocity 1.0 m/s

^c Individual values for steady burning and vigorous boiling periods

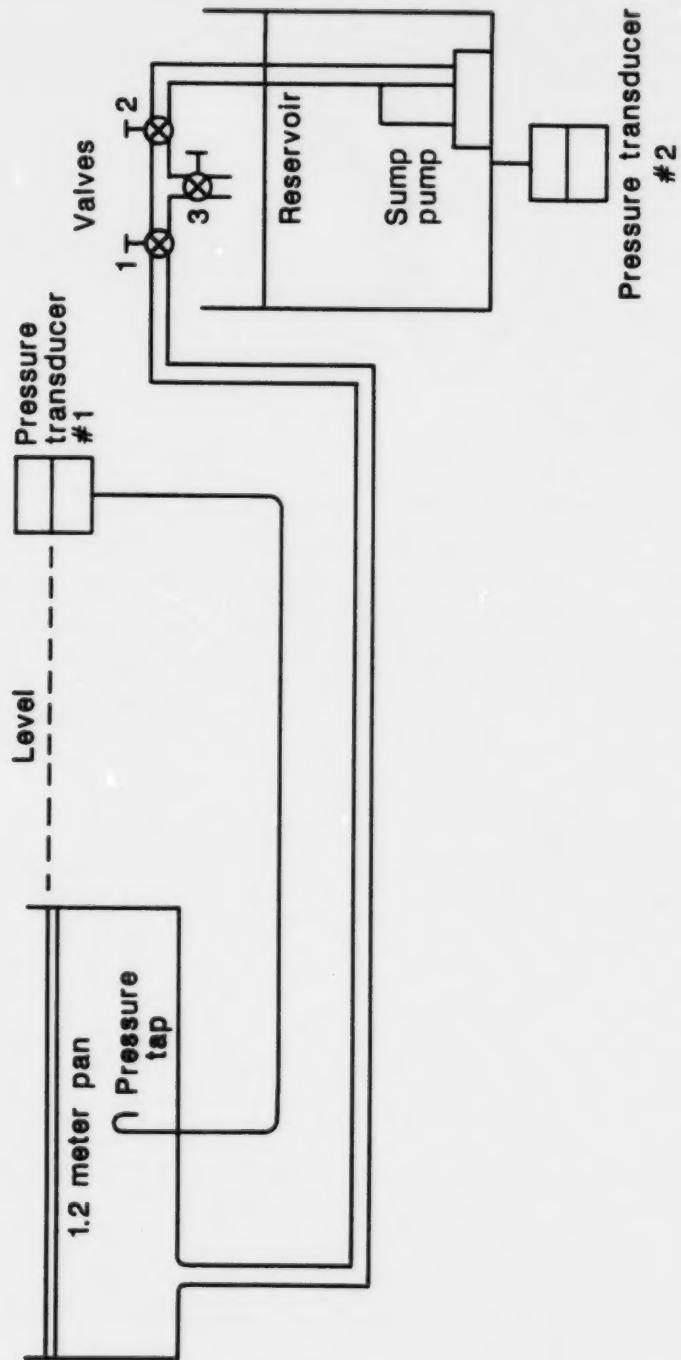


Figure 1. Schematic diagram of the fuel level control device.

permit water to flow from the sump pump in the auxiliary reservoir so as to restore the initial test pan pressure. The decrease in the weight of water which is recorded as the output of pressure transducer No.2, corresponds to the fluid volume required to maintain the prescribed depth in the test pan. Since the oil in the pan is less dense than water, a slight error (averaging about 8% of the oil depth) will be introduced unless compensated by a predetermined amount based on the oil thickness and the difference in specific gravities of oil and water. Although not compensated for during the test the effects of density difference were included in the calculation of burning rate.

Figure 2 is an example of the recorded weight of water supplied in Test A12 (from output of pressure transducer No.2) and illustrates the increased burning rate during the vigorous burning period near the end of the test.

The recorded energy release rate for the Alberta Sweet crude followed the same pattern as in earlier tests, i.e. a rapid rise to approximately 1.25 MW followed by a slight decrease over a 1.5 min period to about 1.0 MW and then rising to a peak value of about 2.5 MW during the vigorous burning period (see Figure 3). The pure compounds toluene and n-decane did not display the same changeover to intense burning and corresponding water-boiling phenomenon as the Alberta Sweet crude although there was noticeable boiling for an extended period over the surface of the decane. This is ascribed to the much higher oil surface temperature (corresponding to the higher boiling point) for the crude oil at this stage of burning. The decane energy release rate increased fairly steadily to a peak of 2.3 MW followed by a steady decline whereas the toluene approached and maintained a steady-state energy release rate of only 1.6 MW. Both the toluene and the decane were observed to burn as flame sheets around the perimeter of the test pan with very little or no flaming at the central core. This is ascribed to the greater vapor production rate for the pure hydrocarbons. In the case of toluene, flame lifting at the rim was quite pronounced; this may be seen in the close-up photograph of the liquid surface in Figure 4.

As shown in Figure 5, the recorded peak level of radiant energy feedback to the center of the liquid surface was lowest for toluene (23 kW/m^2) and highest for the Alberta Sweet crude (65 kW/m^2). As noted in the previous report [1], the feedback radiation did not follow the same temporal pattern as the energy release rate, and this is in part a consequence of the different quantities of smoke generated which affects both the absorption of radiation by and the emission of radiation from the flames. Also shown in Figure 5, for direct comparison with the feedback at the center for Alberta Sweet crude, is the recorded level of radiation energy feedback near the rim of the pan. At levels of radiant energy feedback below approximately 10 kW/m^2 , flaming could not generally be sustained.

The recorded smoke obscuration in the stack (see Figure 6) confirms graphically the visual test observations in which very little smoke was noted throughout the test for the decane and very heavy smoke for the toluene. The progressive increase in smoke generation for the Alberta Sweet crude can be attributed to the changing composition of the crude oil toward the heavier fractions with decreased combustion efficiency.

The measured oil surface temperature provides a good indication of the pattern of burning. In Figure 7, are plotted the temperatures at the oil surface near the rim where the fuel vapor from the burning liquid and air are

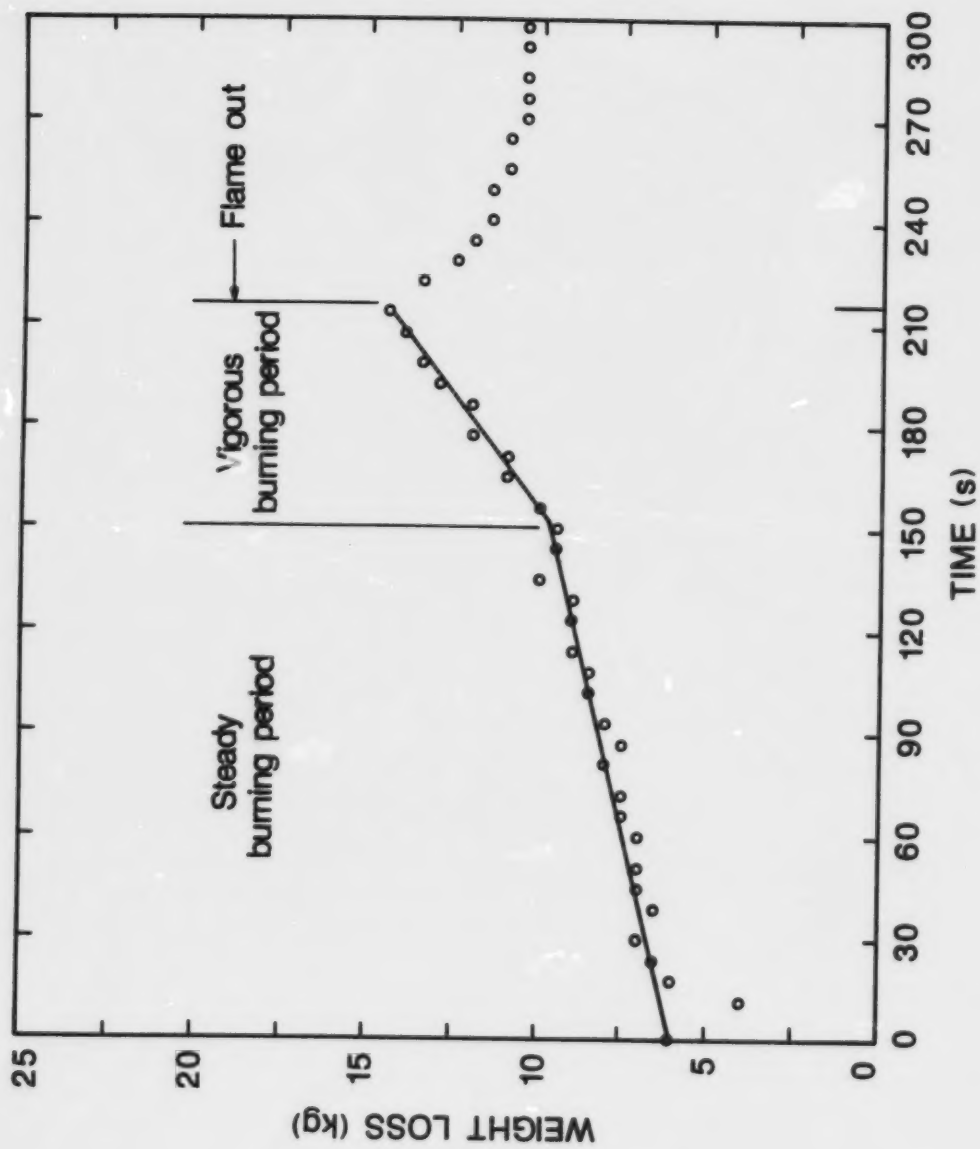


Figure 2. Recorded Weight of Water Supplied to maintain oil level (Test A12).

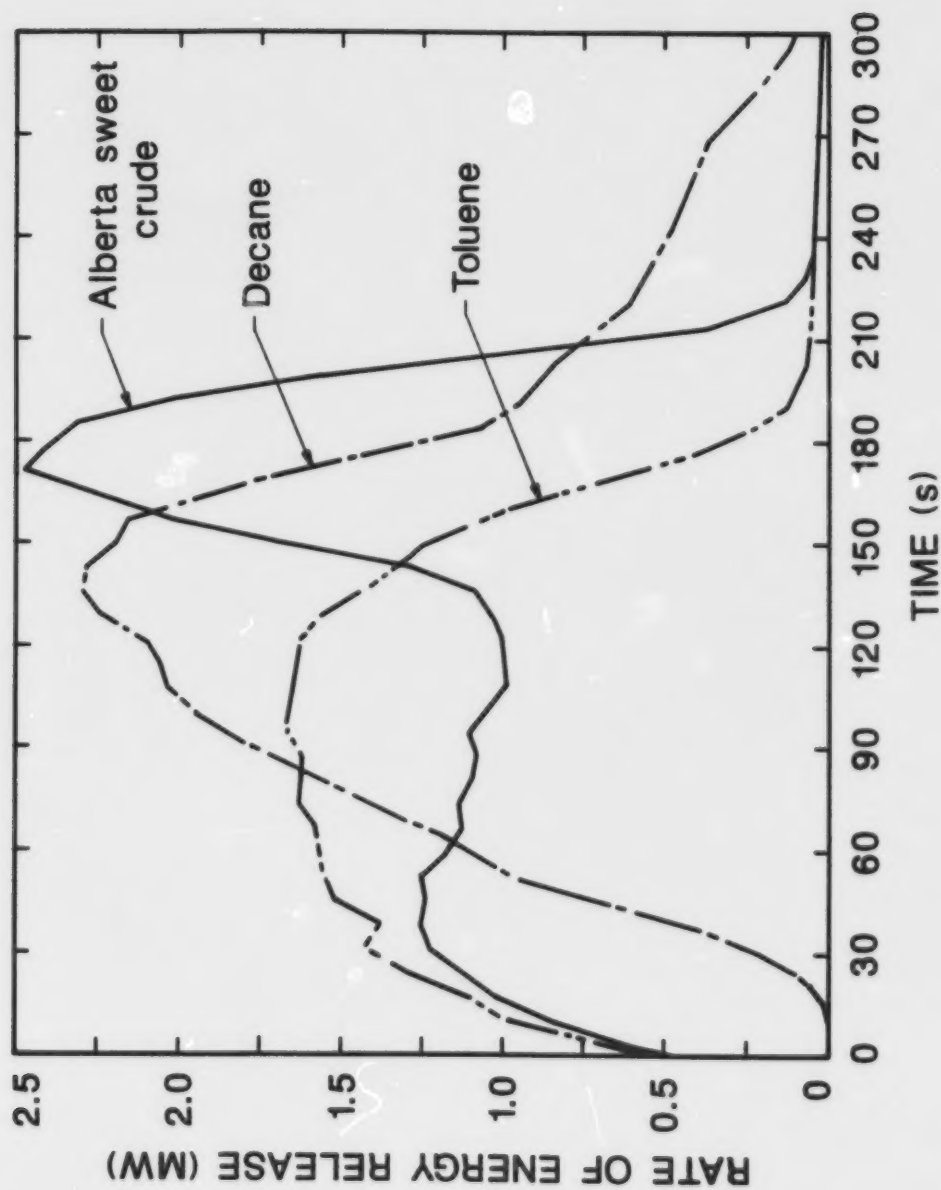


Figure 3. Energy release rate for Alberta Sweet crude oil and pure hydrocarbons (10mm layer thickness).



Figure 4. Steady burning of toluene showing flame lifting.

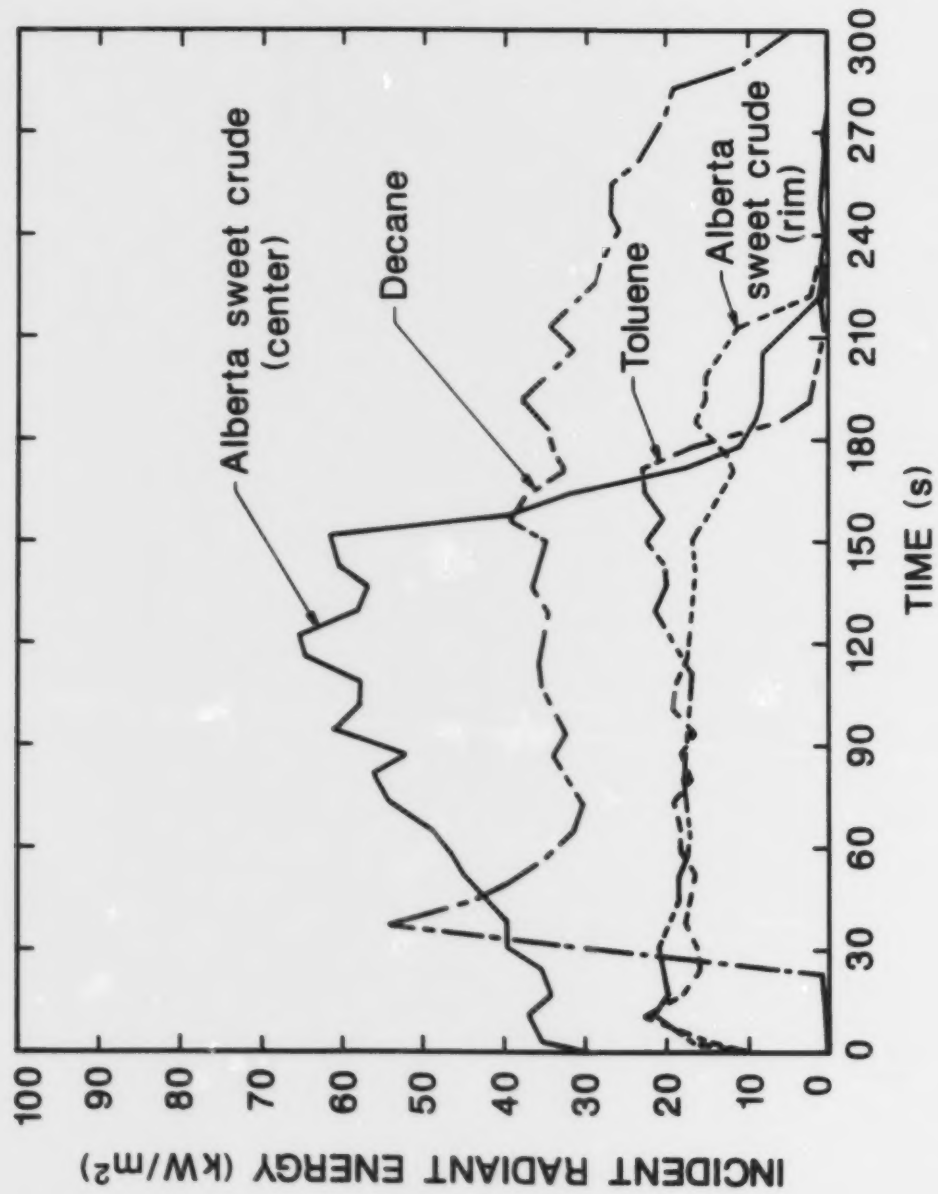


Figure 5. Radiant energy feedback to the fuel surface.

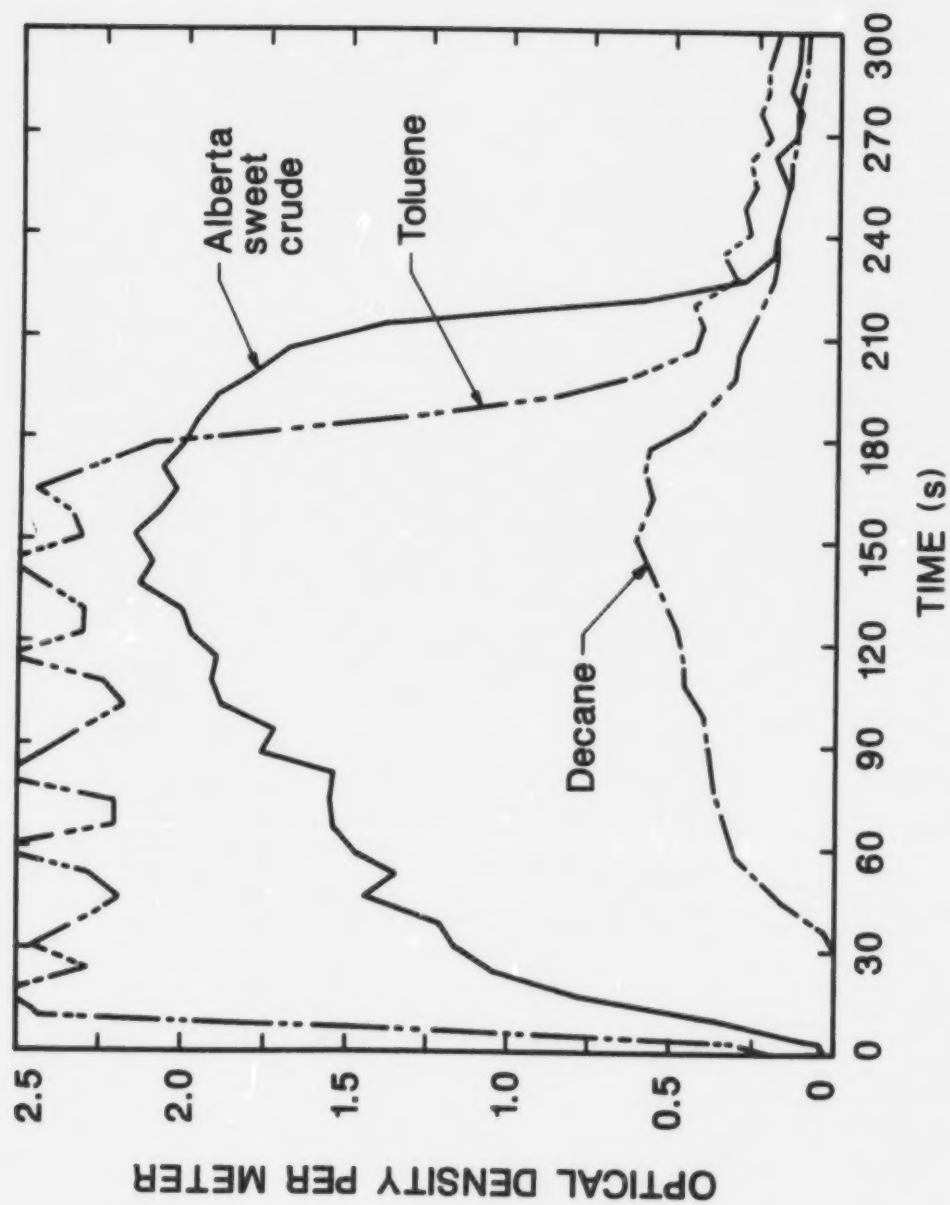


Figure 6. Smoke obscuration in stack.

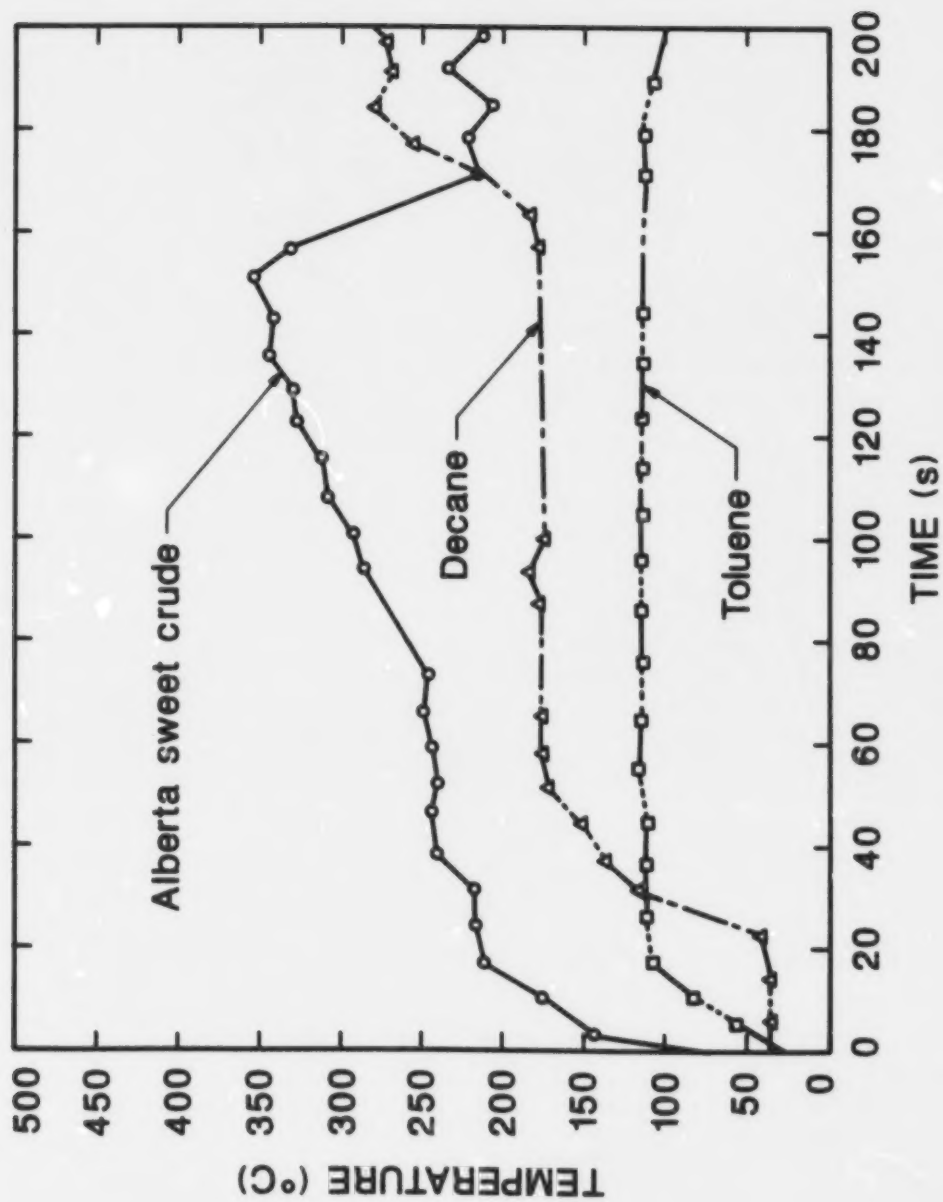


Figure 7. Oil surface temperature at rim.

able to mix to produce the basic flame structure. The constant temperature portions correspond to the boiling points of 111 °C for toluene and 174 °C for decane are clearly observed. The steadily increasing oil surface temperature for the Alberta Sweet crude demonstrates the progressive boiling of the heavier fractions which have higher boiling points. This is a reasonable and expected behavior, in contrast to a constant temperature phenomenon [2].

Using the previously described thermocouple rakes [1], temperature measurements were recorded within the oil layer, in the fuel-rich vapor above the oil, and in the water sublayer. This provided temperature profile data at selected times such as that shown in Figure 8 for three liquids at 115 sec, where the measured data points were connected by straight line segments. However, due to the uncertainty in establishing the free surface of the liquid closer than ± 1.6 mm, the temperature profiles may appear slightly displaced relative to the original oil surface. These data illustrate that at the center of the pan, the temperature immediately at and above the surface of the toluene is 111 °C corresponding to toluene at its boiling point. Likewise, the space directly above the boiling decane liquid consists of decane vapor at 174 °C. At 115 seconds, these pure compounds are in the middle of the characteristic steady burning phase and the flames are mainly confined to an envelope close to the rim where air is available for burning. At the same time in the burning period of the Alberta Sweet crude (115 sec), the oil surface has reached a temperature of approximately 250 °C to 300 °C and is continuing to increase steadily as the lower boiling point fractions disappear.

The main effects of a 1 m/s or 2.5 m/s wind blowing across a burning pool of Alberta Sweet crude was (a) to deflect the flames as much as 45° from the vertical and (b) to increase the burning rate and reduce the burning time noticeably (see table 1). The increased burning rate is attributed to the increased availability of oxygen even though the deflected flame configuration would otherwise provide less radiation feedback to the oil surface.

Over the initial water temperature range explored (5 °C to 28 °C), there was no pronounced, systematic effect on measured temperature in the flame, thermal radiation, burn time or residue remaining. This is not surprising since the heat loss by conduction is relatively small and occurs in a thin surface layer so that the cooler substrate has negligible effect until burning is nearly complete.

Energy Balance

For estimating the energy balance, discussion will be limited to the quasi-steady burning period prior to the violent burning phase involving the boiling of the water sublayer. Even so, conditions at the burning oil surface, plus the attendant uncertainties in experimental measurement of irradiance, and of temperature and level control within a few millimeters, provide a severe measurement and analytical challenge. In the violent burning stage, this is further complicated by the motions of boiling water and splattering oil droplets, possibly resulting in water-oil emulsions.

In simple qualitative terms, the net rate of energy received at the oil surface may be equated to a series of energy rate terms:

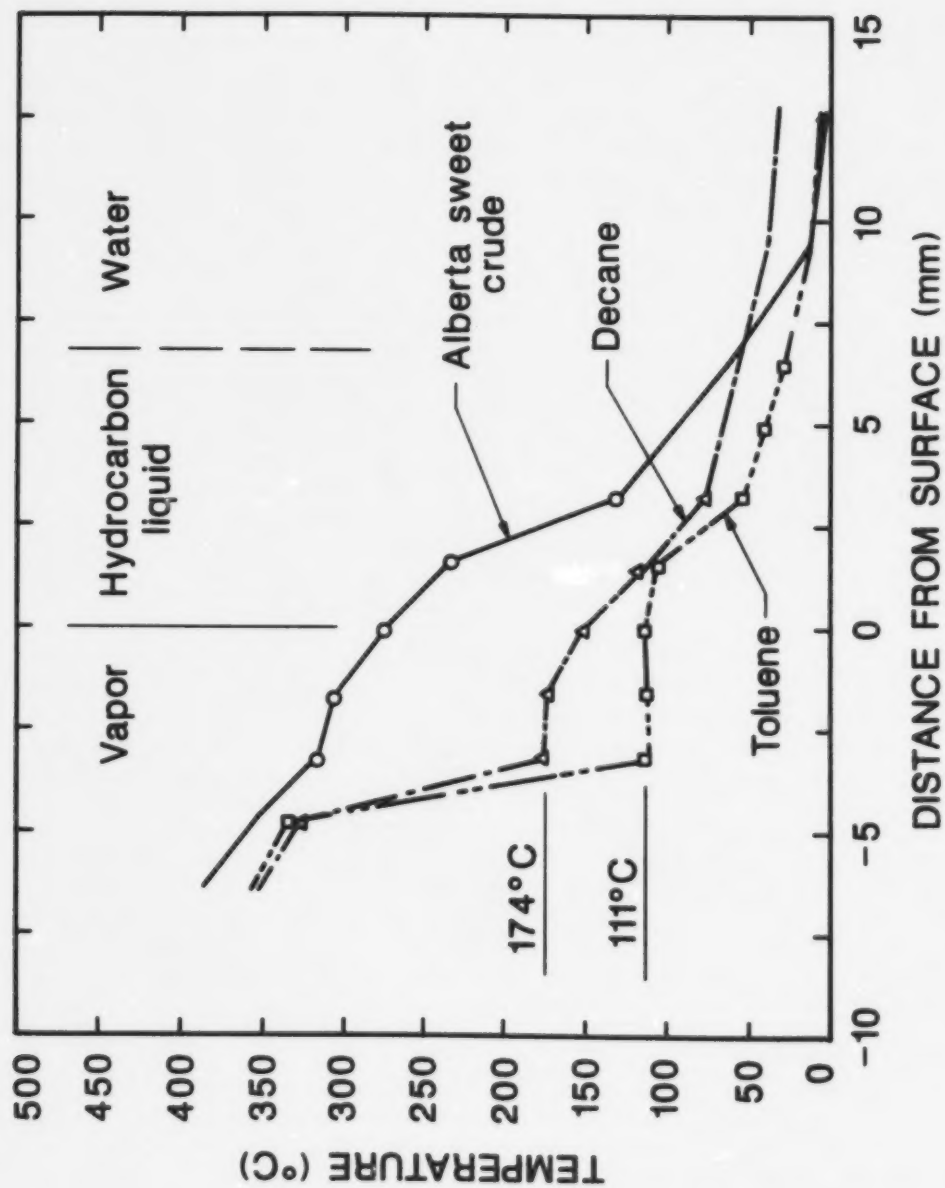


Figure 8. Temperature profile at center of pan ($t=115$ seconds).

$$Q_i - Q_{rr} = Q_v + Q_c$$

where Q_i is the rate of radiant energy incident on the oil surface, Q_{rr} is the rate at which energy is reflected or re-radiated, Q_v is the energy flux required to vaporize the oil, and Q_c is the net energy flux conducted or convected away from the oil surface. Not included here are any energy gains or losses associated with the vessel walls.

In order to make energy balance estimates, thermal properties of the test liquids are required. Values were either obtained or derived from available reference sources and are listed in Table 2.

During the quasi-steady burning period, the radiant energy flux incident on the surface of the Alberta Sweet crude oil at the center was found to rise from 40 to 65 kW/m² whereas the radiant flux energy at the rim remained fairly constant at 18 kW/m². It is not clear if the mean levels of radiant energy flux within a much larger pool would be closer to the values at the center or at the rim. Although the rate of energy reflected and re-radiated is important, this could not be estimated due to lack of data on spectral and total absorptivity.

From the recorded temperature profiles, temperature gradients at the oil surface were determined and estimates made of the extent of heat conduction to the interior of the oil. As shown in Table 3, the maximum temperature gradient in the oil was 29 degrees C/mm corresponding to a heat loss by conduction of 2.5 kW/m². The accuracy of this measurement is estimated to be ± 20 percent. For estimating the thermal conductivity of the Alberta Sweet crude, an average boiling point of 250°C was selected for the steady-state burning period. Also listed in Table 3 is the energy rate required to vaporize the oil as computed from the measured liquid regression rate and the heat of vaporization at the boiling point. For the Alberta Sweet crude, the heat of vaporization is a changing function since there is a progressive shift from the lowest to the highest boiling point fractions during the burning process. An effective composite heat of vaporization may be estimated if the crude oil is assumed to consist of paraffinic and aromatic components as illustrated in Table 4. In this case the rate of energy required for vaporization during the quasi-steady state burning period is approximately 6.7 kW/m².

If the rate of energy loss is in the form of convection, it may be appreciable. For example, a 3 mm thick layer of crude oil exposed to a temperature difference of 150 °C could transfer approximately 10 kW/m². This is based on a heat transfer coefficient of 0.075 kW/m²K obtained from empirical correlation of convective heat transfer data across a liquid layer.

In the case of the pure liquid hydrocarbons n-decane and toluene, a region of constant temperature approximately 3 to 5 mm thick exists in the vapor zone directly above the liquid surface. However, a constant temperature ("homothermal") liquid layer such as noted by Burgoyne and Katan [3] and by Blinov and Khudyakov [4] was not observed. In their 1947 paper, Burgoyne and Katan suggested that distillation may occur at the bottom of such a liquid layer and that the vapor bubbling up could provide a stirring action (with the required nuclei provided along the vessel walls). For the Alberta Sweet crude oil, no distinct constant temperature liquid layer was discernible. The computed rates of energy conducted into the pure hydrocarbons ranged from 2.3 to 3.3 kW/m², whereas the energy rate required for vaporization varied from 15.1 to 19.1 kW/m². In these cases, it is also not possible to provide a complete and consistent heat balance in the absence of more confirmation on the magnitudes of the energy rate terms associated with convection and with reflection and re-radiation.

Table 2 Properties of Test Liquids (Typical)

Liquid	Grade (Purity) (%)	Boiling Point °C	Density @ 20°C kg/m ³	Flash Point °C	Heat Capac ^a @ mean temp kJ/kgK	Thermal Conduct- ivity ^a @20°C @b.p. W/mK	Heat of Vaporiz'n ^a @20°C @b.p. kJ/kg	Net Heat of Combust ^a MJ/kg
Alberta Sweet		37-350+	840	7	2.34 ^b	0.120 0.0874	305 ^b	43.4 ^b
n-Decane	Techn'l (99)	174	730	44	2.50	0.130 0.0829	354 276	44.2
Toluene	ACS (99)	111	860	5	1.88	0.135 0.110	409 360	40.5

^a For pure toluene, and n-decane, values of k_{20} , k_{bp} , C_p , H_v and H_c are based on data and methods in Technical Data Book - Petroleum Refining, Metric Edition 1977, 1984. For Alberta Sweet crude, k_{bp} is based on laboratory measurements at 20°C and analogous extrapolation techniques at an approximate boiling point of 250°C.

^b Computed on the basis of mass fraction for a simulated blend representing Alberta Sweet crude (Table 4).

Table 3 Energy Balance Estimates for the Steady Burning Period

Test	Liquid	Test Period	Q_i Incident Radiant Energy		Burning Rate	Q_v Energy Reqd for Vaporiza- tion	Surface Temp Gradient	Q_c Heat Conduction Into Oil
			ctr kW/m ²	rim kW/m ²				
		sec			mm/min	kW/m ²	°C/mm	kW/m ²
A12	Alberta Sweet	30-125	40-65	18	1.6	6.7	29	2.5
D01	n-Decane	60-150	34	27	4.5	15.1	28	2.3
T03	Toluene	60-150	19	14	3.7	19.1	30	3.3

Table 4 Composition and Properties of Simulated Crude Oil

Component		Assumed Mass Fraction	Density @ 20°C kg/m ³	Boiling Point °C	Heat of Vaporization @ Boiling Pt kJ/kg	Net Heat of Combustion MJ/kg
C ₅ H ₁₂	Pentane	0.10	626	36	357.2	44.98
C ₁₀ H ₂₀	Cyclodecane	0.75	858	202	286.4	43.82
C ₇ H ₈	Toluene	0.15	867	111	360.2	40.53

Source: Technical Data Book - Petroleum Refining, Metric Edition 1977, 1984

Burning of thin oil layers

Oil spill combustion in which the oil layer is being churned by the boiling of a supporting water layer may be the most prevalent conditions for thin oil slicks and the most beneficial because of relatively lower smoke yields when combustion can be maintained. This type of combustion condition was observed during the latter part of each crude oil burn in this study. Churning of the water and oil interface and possible emulsification eventually leads to flame extinction as the oil is cooled by the mixing process sufficiently to prevent the flame sustaining fuel vaporization. Thus heat transfer processes in this complicated burning situation determine both the amount of water mixed with the oil vapors during the combustion and the amount of oil left on the water surface after flame extinction.

To understand the combustion process better a simple transient conduction model with a specified burning surface temperature was formulated as an attempt to predict the onset of boiling in the water supporting layer beneath the burning oil layer. Experimentation was performed with pure hydrocarbon fuels and three types of crude oil. It was found that there was no reasonable choice of physical properties for this simple combustion model that would consistently predict the onset of water boiling for either a bench scale or large scale pool fire situation. In all cases the calculated time to boiling was much greater than that observed in experiments. A more complete model that includes in-depth radiation adsorption as well as conduction into the liquid is being formulated.

SMOKE CHARACTERISTICS

In the previous study [1], the total smoke particulate and its chemical content were measured for smoke emitted during the steady burning phase for a 30 mm thick layer of Alberta Sweet crude oil on water. While collecting smoke during the steady burning phase simplified the measurements and allowed good repeatability, it ignored the effects of oil layer thickness and boilover on smoke emission. To complete the laboratory scale study of smoke, the effects of oil layer thickness on the total smoke emitted and its chemical content were studied. The procedure for collecting a representative fraction of smoke throughout the entire burning period is described below. In the previous study, we did not include a chemical analysis of the PAH content of the crude oil and in the residue. Such measurements are included in this study to provide the necessary data for assessing the environmental impact of burning crude oil.

As smoke rises in a plume from the burning oil, the individual agglomerate particles will collide and stick together forming larger agglomerates. This process will continue to take place as the smoke plume moves downwind. There is very little information regarding the effect of the agglomeration process on the properties of the smoke. Properties of keen interest in regard to environmental effects are changes in the optical properties of the smoke and the change in the aerodynamic size of the smoke particles. The optical properties are of concern in regard to visibility reduction caused by the smoke and the absorption of solar radiation in the atmosphere. The aerodynamic properties of the smoke are of interest in regard to the deposition of the smoke. As will be discussed in the Particulate Settling Analysis section of this paper, the smoke deposition is affected by the high mass loading of the smoke inducing a cloud settling effect as well as by the settling velocity of

the individual agglomerates near the ground. The design of a Smoke Aging/Dilution facility is described and preliminary results on the effects of agglomeration on the optical properties and the aerodynamic properties of smoke are given.

Smoke Emission Measurements

Smoke samples were collected and diluted using a glass sampling system shown in Figure 9. The smoke was drawn through an isokinetic sampling probe into a dilution section where it was diluted two to one on a mass basis with approximately 0 °C clean air. Diaphragm pumps pulled the diluted smoke through two filter sets arranged in parallel. Each filter set consisted of a teflon¹ filter, 37 mm diameter, followed by a polyurethane foam vapor trap contained in a glass tube 30 mm diameter and 150 mm long. All teflon filters, polyurethane foams and glass tubes were prewashed to remove organic contaminants. The parallel filter sets allowed simultaneous collection of soot and PAH on the two teflon-polyurethane filter sets. Smoke sampling flow rates averaged approximately 10 liters per minute. In contrast to crude oil burns conducted in previously [1], when samples were collected for short periods during the steady state burning phase, smoke was sampled continuously from ignition until burning was completed. In order to collect sufficient mass for analysis, multiple burns were necessary for the 2 mm, 3 mm, and 5 mm oil layer thicknesses. Upon completion of a burn or series of burns, the teflon filters were weighed and sealed in petri dishes, while the polyurethane foam-glass tube combinations were stored in aluminum foil. Both teflon filters and polyurethane foam were then stored under dry ice until ready for analysis. Soot samples for thermal-optical analysis of elemental versus organic carbon content were collected on quartz fiber filters which had been pre-fired at 700°C for 4 hours. The same collection and dilution system was used for the quartz filters except that polyurethane filters were not included downstream of the quartz filters. Because the thermal-optical technique requires much less soot per filter, smoke sampling flow rates averaged about 2 liters per minute.

In addition to the teflon, polyurethane and quartz filters, samples of the crude oil before the burn and the residue after the burn were also collected for chemical analysis. An oleophilic polypropylene batting was used to soak up the burn residue for weighing. The percent of oil burned was calculated based both on the mass loss during the burn and on the mass of the burn residue. Both methods agreed within a few percent except for the 2 mm layer, for which the first method gave 63% and the second method gave 54%. The results of the second method are given in Table 5.

The effect of oil layer thickness on the heat release rate and on the burning in the 0.6 m diameter pan rate are illustrated in Figures 10 and 11. The 5 and 10 mm thick pool burns have a relatively steady burning phase with a 0.2 MW heat release rate followed by rapid burning with a 0.6 to 0.75 MW heat release rate as the water under the oil begins boiling. Apparently the boiling of the water causes small droplets of crude oil to be emitted from the surface. The rapid boiling phase lasts up to about one minute. For the 2 and 3 mm thick

¹ Certain commercial equipment, instruments, and materials are identified in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the materials or equipment identified are necessarily the best for the purpose.

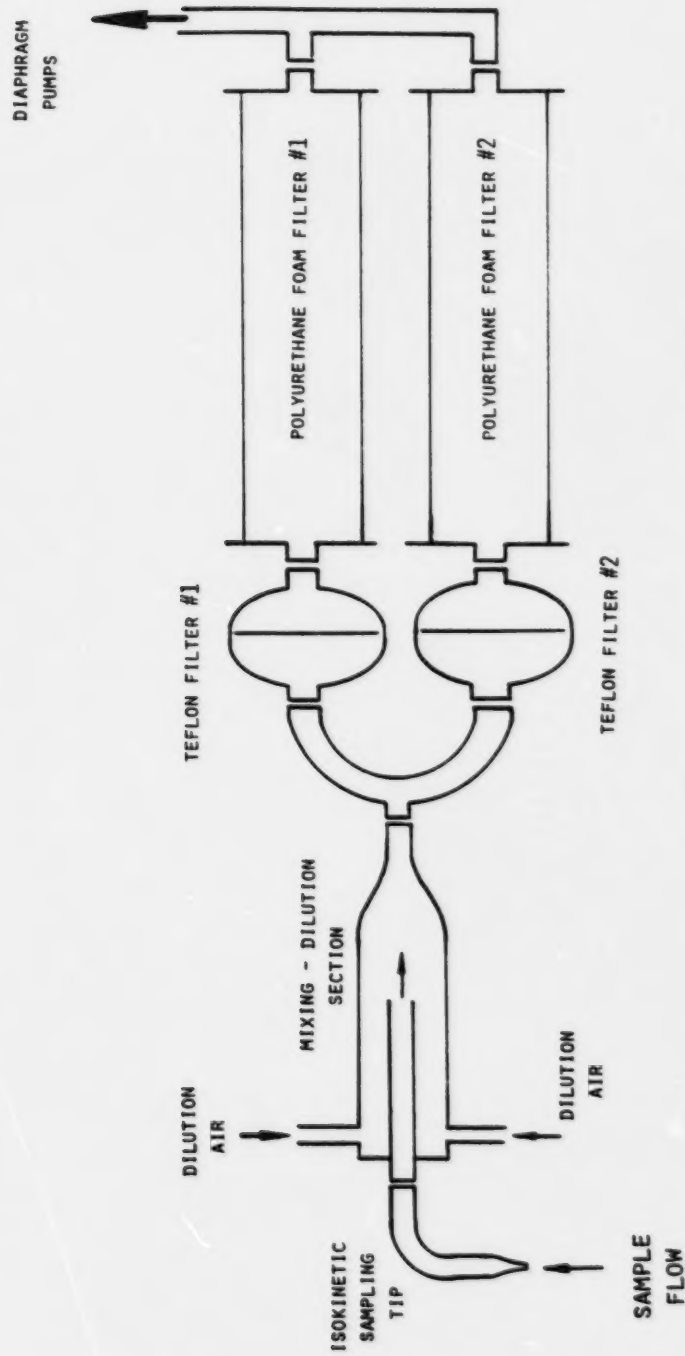


Figure 9. Smoke/PAH sample collection system.

TABLE 5. COMPARISON OF ALBERTA SWEET CRUDE OIL BURNING DATA FOR
0.6 M AND 1.2 M DIAMETER PANS

Oil Layer Thickness mm	Pan Dia. m	Heat Release Rate, MW/m ²		Burning Rate, g/m ² s		% Oil Burned	Time to Boilover s	Effective Heat of Combustion MJ/kg	Burn Time s
		Steady	Peak	Steady	Peak				
2	0.6	-	0.74	-	18	54	35	35	82
2	1.2	-	0.86	-	-	67	-	-	-
3	0.6	-	1.06	-	32	73	38	33	99
5	0.6	0.60	1.90	15	38	76	100	36	151
5	1.2	0.89	1.89	-	-	86	55	-	-
10	0.6	0.67	2.95	15	83	83	271	42	310
10	1.2	1.00	2.51	22	67	92	130	-	-

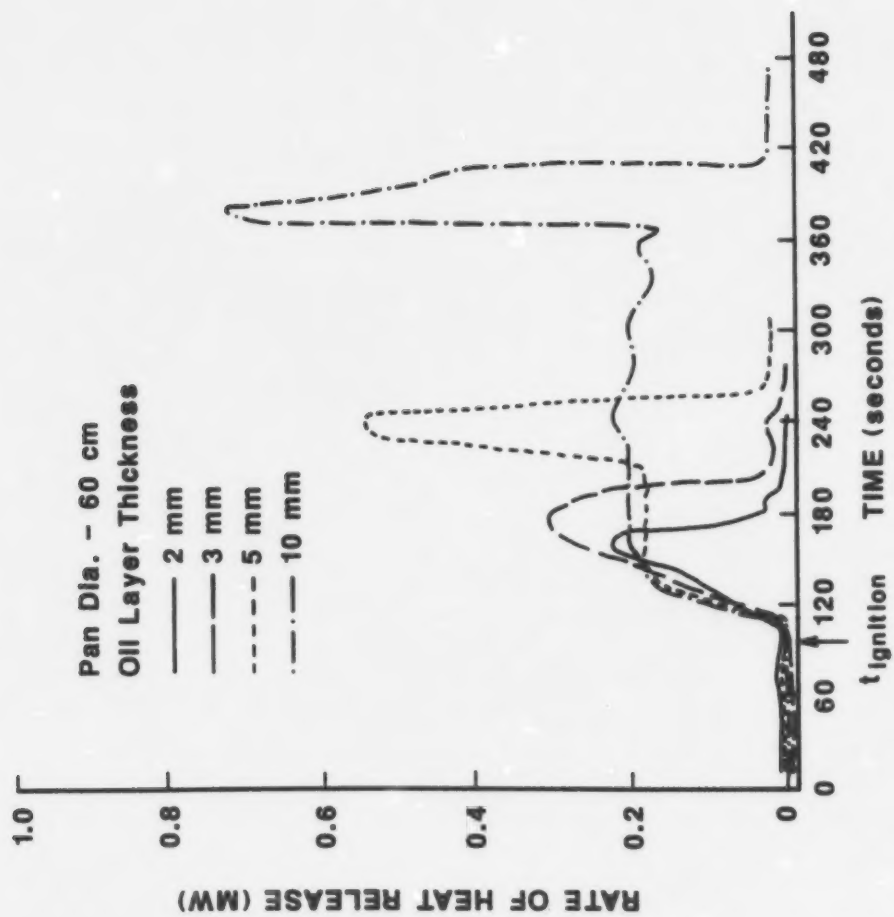


Figure 10. Effect of oil layer thickness on heat release rate for crude oil fires.

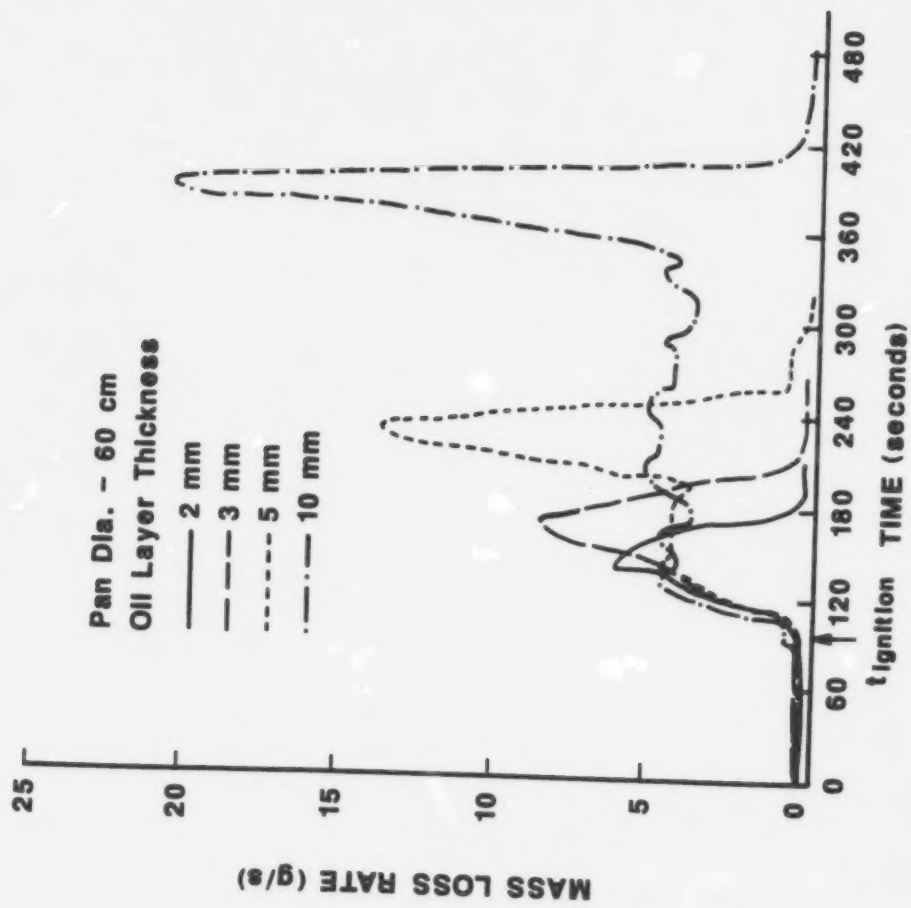


Figure 11. Effect of oil layer thickness on mass loss rate (fuel) for crude oil fires.

layers, there is no steady burning phase. The time to boilover increases with oil layer thickness from about 35 seconds for the 2 mm layer to about 270 seconds for the 10 mm thick layer (Table 5). The smaller the layer thickness, the larger the fraction of the mass loss occurring during the boilover phase. While the heat release rate varies with layer thickness and time, the effective heat of combustion is relatively constant throughout each test and over the ranges studied with a value of 35 to 40 MJ/kg. This represents 80% to 92% of the estimated net heat of combustion, 43.4 MJ/kg.

A comparison between these results for a 10 mm thick layer in an 0.6 m pan and the results for a 1.2 m diameter pan [1] are contained in Table 5. The steady state heat release rate for the 1.2 m diameter pool, 1.00 MW/m², is about 50% greater than for the 0.6 m diameter, 0.67 MW/m². The mass burning rate shows a similar trend increasing from 15 g/m²s to 22 g/m²s with increasing pool size. This result is expected in view of the relationship between burning rate and pool diameter established by Blinov and Khudyakov [4] and analyzed by Hottel [5]. Other noteworthy effects of pool size include a smaller residue percentage at the larger pool size and a significantly shorter time to boilover, 130 seconds for 1.2 m diameter pool, compared to 271 seconds for the 0.6 m diameter pool with 10 mm layer depth. About 60% of the mass loss occurred during boilover for the 1.2 m pool compared to only about 33% for the 0.6 m diameter pool.

The time dependence of the smoke extinction, k , for a wavelength $\lambda=633$ nm is illustrated in Figure 12 for a 10 mm oil burn. In the region where the mass loss rate of the fuel is a maximum, the smoke extinction coefficient k is actually decreasing. It appears that the smoke emission is greatly reduced during this rapid burning phase. The quantity σ_f , the extinction cross section per unit fuel mass loss, is a convenient relative measure of the smoke emission.

$$\sigma_f = k/(\dot{m}_f/\dot{V}),$$

where $\dot{m}_f$ is the fuel mass loss rate and $\dot{V}$ is the volumetric flow rate through the duct. The quantity σ_f is proportional to the smoke yield ϵ , defined as the mass of smoke aerosol produced per gram of fuel consumed. The plot in Figure 12 clearly shows a dramatic decrease in σ_f by about a factor of five during the rapid fuel burning. This effect of decreasing σ_f at the time of the maximum burning is observed for all layer thicknesses.

The smoke yield results are summarized in Table 6. It is seen that the smoke yield ϵ increases by more than a factor of two from 0.035 to 0.080 as the fuel layer thickness is increased from 2 mm to 10 mm. The value of σ_f also increases by almost a factor of two from 0.33 m²/g to 0.65 m²/g as the thickness is increased from 2 mm to 10 mm. The quantity σ_s , which is the specific extinction cross section per unit mass concentration of smoke, is in the range 7 to 9 with no definite dependence on oil layer thickness. The experimental variability is larger in these experiments compared to the steady state experiments performed last year because of the large change in burning rate and smoke emission during the burn. Also, there is evidence of large oily droplets on the sampling probe and just downstream of the bend in the sampling probe. These droplets may flow through the laser beam, but possibly only a small fraction are making it to the filter.

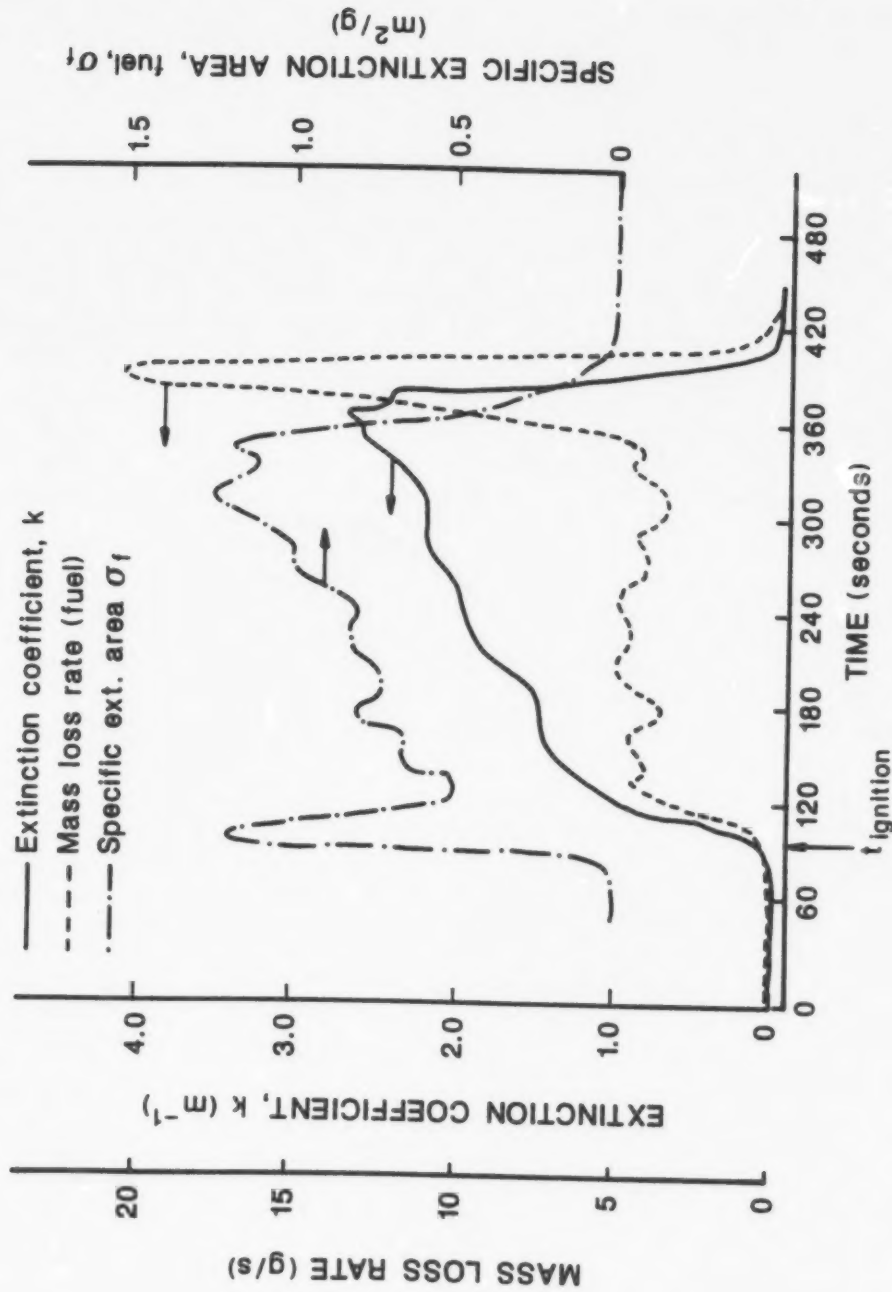


Figure 12. Mass loss rate and extinction coefficients versus time for a crude oil fire.

Chemical Analysis

Smoke samples were collected on quartz filters as described in the preceding section and sent to a contract laboratory for the thermal-optical analysis for organic/elemental carbon [6]. The organic fraction of the sample is determined by heating the sample in pure helium in four temperature steps up to 770 °C. The remaining carbon, the so called elemental carbon, is then oxidized by introducing 2% O₂ into the gas stream. The elemental carbon fraction of the smoke was in the range 79% to 86% without any significant trend

TABLE 6. EFFECT OF LAYER THICKNESS ON SMOKE EMISSION
FROM ALBERTA SWEET CRUDE OIL
(60 cm diameter pan)

Oil Layer Thickness mm	Average Burning Rate g/s	Smoke Yield g/g	k m ⁻¹	σ_f m ² /g	σ_s m ² /g
2	2.2	0.035	0.39	0.33	9
3	3.9	0.050	0.96	0.48	7
5	5.6	0.080	1.43	0.51	7
10	5.3	0.080	1.75	0.65	8
30 ^a	5.1	0.100		0.88	9.4

^a The mass loss and smoke measurements correspond to the steady burning phase.

with oil layer thickness. The heavier deposits were observed to be very uneven across the filter surface. These results are to be compared with values over 90% obtained for the collection of smoke last year from the steady burning phase. This year the samples were collected over the entire burn. The lower values observed in this years study may be a result of fuel droplets being emitted from the surface and collected during the rapid boiling phase.

The PAH analyses of 11 filter and corresponding polyurethane foam samples were performed by the Center for Analytical Chemistry at NBS and by Environment Canada at Ottawa. In addition, PAH analyses were performed on 5 crude oil samples and on 7 burn residue samples. The goal of this portion of the research was to assess the effect of oil layer thickness on the PAH emission and on the PAH content of the residue. The sample procedure was essentially the same as described previously reported [1]. The teflon filters and polyurethane foam samples at NBS were spiked with appropriate amounts of an internal standard solution containing phenanthrene-d₁₀ and 1-n-butylpyrene. Agreement within about 10% was obtained between the concentrations calculated using the two standards suggests that there were no significant losses of the more volatile species relative to the less volatile standard, 1-n-butylpyrene.

The analysis at NBS involved gas chromatography with flame-ionization detection. Extensive pre-separation using liquid chromatography was necessary to isolate the PAH-rich fraction when using this method [7]. At Environment Canada, mass detection is used for quantifying the individual PAH species, which has the advantage of requiring a minimum amount of pre-separation. A total of five internal standards are used for accounting for the variability in the recovery factor with the size and structure of the PAH. One advantage of

the GC/FID system for the nominally 10 mg smoke samples is its factor of 10 higher sensitivity than the mass detection method.

Essentially the same preparation method was used for the crude oil and oil residue samples except that the silica cartridges were not used in the pre-separation procedure. The results for the crude oil and residues are summarized in Table 7. Generally, the PAH content in the crude and the residue were similar, which is more apparent when comparing the chromatograms for the oil and residue (see figure 13). Over 90% of the PAH content are three membered rings with high concentrations of phenanthrene, methylphenanthrene, and dimethylphenanthrene. Environment Canada found that the concentrations of four and five membered rings were less than the three membered ring by a factor of 10 or more. The recovery percentages for the spiked components were uncertain because of interferences. The GC/FID method used at NBS was unable to quantify PAHs with more than 3 rings due to the complicated structure in the chromatogram in this region. Both laboratories agreed to within 10 - 20% for the concentration of phenanthrene, which was the only PAH in the oil samples measured by both laboratories.

Table 8 includes the masses of six PAHs measured in the extracts of five polyurethane foam plugs positioned downstream of the teflon filter. These results would include both PAH inherently in the vapor phase, as well as those species that were desorbed from the particles on the filter and subsequently collected on the foam. The top and bottom sections of PU-12 were processed separately to determine whether any breakthrough of PAH had occurred. No significant concentration of any PAH was observed in the bottom section, suggesting that PAH breakthrough was not a problem in this study. Comparison of the masses of PAH in the foam and filter extracts shown in Table 8 indicate that a major fraction of three of the PAHs, all three ring compounds, were collected in the vapor phase. The agreement between the two laboratories was within the 10 - 20% measurement uncertainty as indicated by the good agreement between the results by NBS on sample 5 and the results by Environment Canada on sample 6, which was collected simultaneously with 5 and had almost the same filter mass. The distributions between particle and vapor phase were sample dependent with the smaller layer burns having a larger vapor component. The cause of this sample dependence is probably desorption of the PAH, since the total collection times were three to five times longer for the 2 mm and 3 mm burns compared to the 5 mm and 10 mm burns. An individual burn was shorter for the 2 and 3 mm burns but many burns (12 mm for the 2 mm layer and 7 mm for the 3 mm layer) were required to obtain enough smoke sample for analysis. If one combines the results for the vapor and the particulate phases, there is no systematic effect of layer thickness on the 3 ring PAH content.

The results on the total PAH, both in the particulate and vapor form, per unit smoke mass are contained in Table 9. There is some variability from sample to sample but no obvious dependence on the layer thickness. That is, both the total amount of the PAH and the type of PAH appears to be independent of the thickness of the layer being burned. The results are also similar to the results for the collection of the smoke during the steady burning of a 30 mm pool carried out last year. The concentration of phenanthrene and anthracene are low for the 30 mm burn, but this is to be expected, since only the particulate was collected in this sample. The low concentration of methylphenanthrene relative to phenanthrene indicates that 10% or less of the smoke is unburned crude oil. This result is consistent with the high elemental carbon fraction of the smoke discussed above.

In Table 10, all the results are summarized on a per gram of crude oil consumed basis for ease in estimating the environmental impact. It is

TABLE 7. CONCENTRATION OF PAH IN ALBERTA SWEET CRUDE OIL AND ITS BURN RESIDUE

PAH	Crude oil "Q"	Crude oil "S"	$\mu\text{g PAH/g sample}$ Residue oil 2 mm layer	Residue "D" 5 mm layer	Residue "Z" 5 mm layer	Residue "Y" 10 mm layer
Acenaphthylene	13		54	26		
Acenaphthene	57		15	10		
Fluorene	59		47	35		
2-Methyl fluorene	147		112	164		
Phenanthrene	150	147	143	129		122
Methylphenanthrene	-	271	-	-		330
Dimethylphenanthrene	-	497	-	-		524
Anthracene	11		19	13		
Fluoranthene	6		22	11		
Pyrene	17		30	25		
1-Methyl Pyrene	39		16	19		
Benzo[ghi]fluoranthene	-		1	2		
Chrysene/Triphenylene	30		24	34		
Benzo[b]fluoranthene	4		7	2		
Benzo[e]pyrene	5		6	6		
Benzo[a]pyrene	-		4	3		
2-Methyl cholanthrene	3		3	3		
Benzo[ghi]perylene	-		2	-		
Total PAH	541	915	505	482		975

1 Samples S and Y were analyzed at the National Bureau of Standards and samples D, K, and Q were analyzed at Environment Canada.

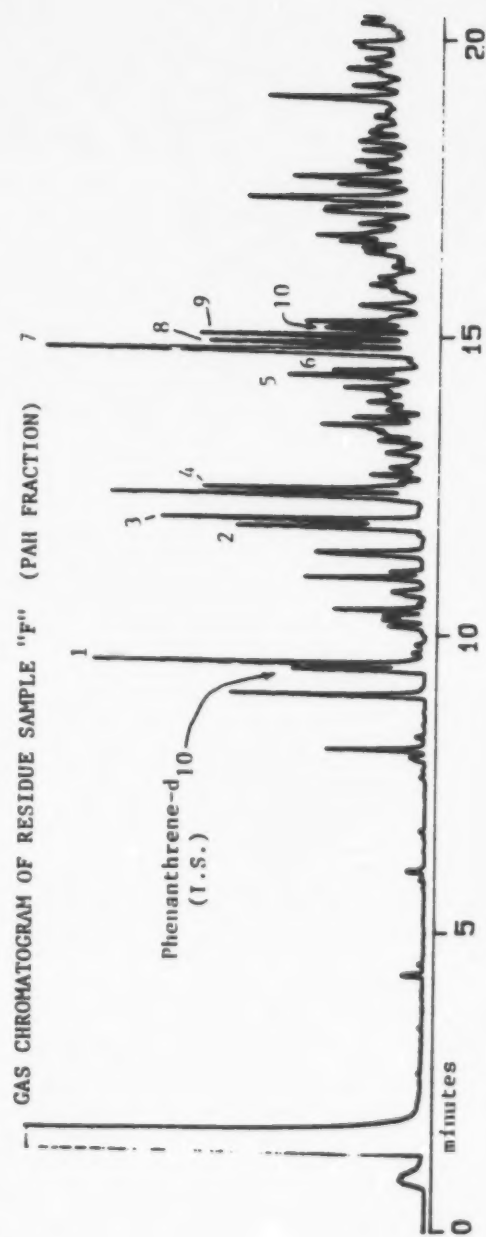
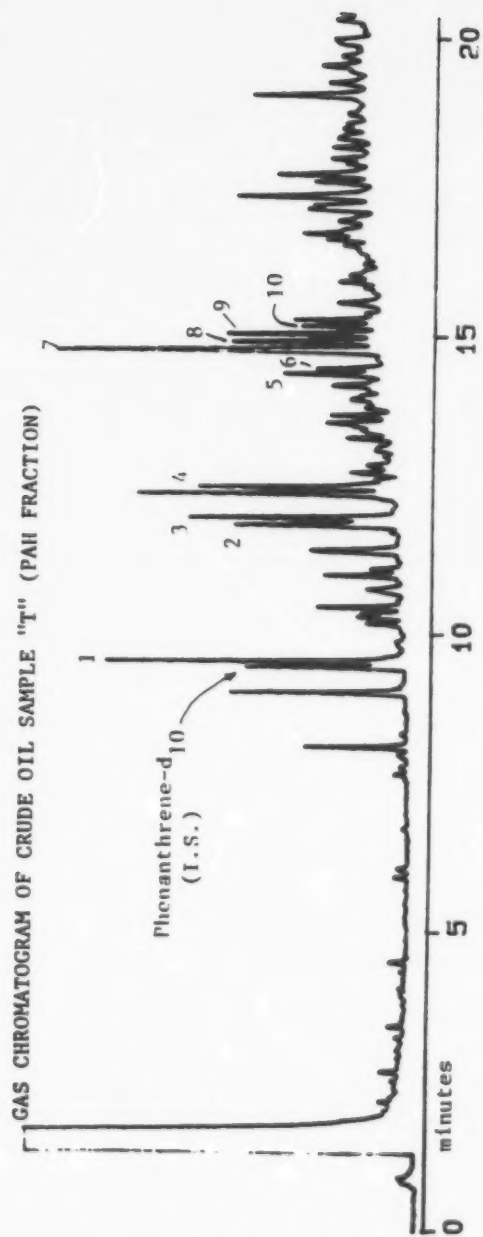


Figure 13. Comparison of gas chromatograph for Alberta Sweet crude oil and residue. Peaks: 1 Phenanthrene, 2-4 Methylphenanthrenes and 5-10 Dimethylphenanthrenes.

TABLE 8. CONCENTRATIONS OF SIX PAHS COLLECTED IN THE VAPOR AND PARTICULATE PHASES FROM THE COMBUSTION OF ALBERTA SWEET CRUDE OIL

Sample	Acenaphthylene	Phenanthrene	μg in extract			Acphenanthylene	Pyrene
			Anthracene	Fluoranthene			
7 2 mm layer							
T-07 ¹	-	1.5	0.4	2.5	-	2.9	
PU-07 ²	13.0	8.9	2.3	1.8	-	1.6	
‡ in vapor	100	86	85	41	-	35	
9 3 mm layer							
T-09	-	3.2	0.7	4.9	3.0	6.2	
PU-09	-	12.6	3.0	2.3	1.0	2.2	
‡ in vapor	-	80	82	32	24	26	
12 5 mm layer							
T-12	-	4.7	1.0	0.5	0.2	0.5	
PU-12	-	3.3	1.0	4.3	2.5	5.2	
‡ in vapor	-	59	50	11	8	9	
5 10 mm layer							
T-05	-	9.0	2.7	9.4	5.3	10.6	
PU-05	-	10.2	2.0	0.2	0.1	0.2	
‡ in vapor	-	53	43	2	1	2	
6 10 mm layer							
T-06	-	7.2	2.5	9.7	-	9.8	
PU-06	25.3	11.1	3.1	0.3	-	0.3	
‡ in vapor	100	61	56	3	-	3	

¹ Teflon filter samples (particulate phase). Samples 5, 9, and 12 were analyzed at the National Bureau of Standards and samples 6 and 7 at Environment Canada.

² Polyurethane foam samples (vapor phase).

TABLE 9. CONCENTRATION OF PAH PRODUCED BY THE COMBUSTION
OF ALBERTA SWEET CRUDE OIL

PAH	2 mm, T-07 & PU-07	3 mm, T-09 & PU-09	5 mm, T-12 & PU-12	10 mm, T-05 & PU-05	30 mm, C-5 #1
Acenaphthylene	1740	-	-	-	-
Phenanthrene	1400	1610	910	1820	910
Anthracene	360	400	210	440	260
Methylphenanthrene	-	49	100	110	-
Fluoranthene	580	770	590	950	700
Acphenanthrylene	-	410	330	520	380
Pyrene	610	890	680	1070	900
Benzo[a]fluorene	70	-	-	-	-
Benzo[b]fluorene	70	-	-	-	-
1-Methyl pyrene	56	-	-	-	-
Benz[a]anthracene	155	200	160	260	220
Chrysene/Triphenylene	78	230	170	260	220
Benzo[b,j+k]fluoranthene	-	370	260	430	380
Benzo[a]fluoranthene	-	120	81	130	-
Benzo[b]fluoranthene	410	-	-	-	-
Benzo[ghi]fluoranthene	160	-	-	-	-
Benzo[e]pyrene	110	120	90	140	120
Benzo[a]pyrene	230	260	190	310	240
Perylene	56	19	35	5	42
Indeno[1,2,3-cd]pyrene	200	180	120	200	190
Benzo[ghi]perylene	120	220	160	250	210
Coronene	-	250	45	190	-
Total PAH	4670(6410 ³)	6100	4130	7090	4770

1 Uncertainties estimated to be about $\pm 10\%$ of the tabulated concentration.

2 These results are taken from the 1987 report [1] based on sample collected during steady burning before boilover.

3 The value in parentheses includes acenaphthylene.

TABLE 10. COMPARISON OF PAH CONTENT OF CRUDE OIL, OIL RESIDUE,
AND SMOKE PER GRAM OF FUEL CONSUMED

Sample/layer thickness	3 rings	3 rings/ methyl	4 rings	4 rings/ methyl	5 or more rings/methyl	5 or more rings/methyl	Total
ALBERTA SWEET	290	910	53	39	9	3	1310
Residue							
2 mm	128	383	35	7	10	1	560
3 mm							330 ¹
5 mm	90	200	25	5	3	1	320
10 mm							230 ¹
Smoke ²							
2 mm	62(123) ³	2	69	2	71	-	210(330)
3 mm	101(210)	2	135	4	112	-	350(460)
5 mm	90(188)	8	126	4	105	-	330(431)
10 mm	181(313)	9	227	11	200	-	628(760)
30 mm ⁴	149	-	241	-	189	-	580

¹ The overall estimates for the 3 mm and 10 mm layers are based on the results for the 2 mm and 5 mm layers and the measured residue fraction.

² By combining the results from NBS and Environment Canada, the PAH concentration for all the PAHs from acenaphthylene to coronene (see Table 5) are included.

³ The values in parentheses include acenaphthylene.

⁴ The smoke collection for the 30 mm pool was for only the steady state burning. Also, the PAH vapors were not collected.

noteworthy that the burning of one gram of crude oil produces less total PAH (the sum of the residue plus smoke/vapor) than is in the original crude oil. However, the concentration of PAHs with 5 or more rings, which includes benzo[a]pyrene, is 10 to 20 times greater in the smoke compared to the fuel. The crude oil and the residue have the same relative concentration of the various classes of PAHs, and the reduction in the overall amount arises from the fraction of the oil burned. While about 90% of the PAHs for the oil and residue have three rings, the PAH content of the smoke/vapor is equally divided among three rings, four rings, and 5 or more rings. The low total concentration of PAH at small layer thickness is primarily the result of the relatively low smoke yield under these conditions. While the smoke/vapor emission is a minimum for the smallest thickness, the residue is a maximum.

Aging and Dilution Chamber

In a smoke plume, the optical and physical properties of smoke change as the smoke ages. Close to the fire source, these changes occur in hot, fresh smoke, but downstream in the plume, changes also occur in the cooler smoke which may or may not be diluted. In order to study how these changes affect properties, such as the light extinction and size distribution of the smoke particles, an Aging and Dilution chamber has been designed. For the hot, fresh smoke, the smoke box must rapidly capture a sample and age it at the collection temperature and pressure for several hours while measurements are collected. For cooler, more diluted smoke, the chamber must dilute a warmer smoke sample and age it at steady conditions until measurements are taken. While the fresh samples require a heated box, the cooler samples need an efficient dilution system. Both samples require a chamber that can be tightly sealed after a sample has been rapidly pulled into the box. The design must include windows for light transmission measurements and sampling ports for mass and number concentration and size distribution determinations. Instead of adding makeup air as the samples are withdrawn and diluting the smoke sample, the chamber includes a large volume piston which moves down to compensate for the sample volume extracted. All these requirements for aging fresh, hot smoke and cooler, dilute smoke are incorporated in the design of the Aging and Dilution Chamber (see Figure 14).

The chamber is a 1 m³ aluminum box which has been lined with stainless steel to reduce corrosion from the hot combustion gases. Forty eight mica resistance strip heaters are attached to the aluminum walls which evenly distribute the heat for wall temperatures up to 150 °C. The intake duct work and valve can also be electrically heated. For experiments which require cooler or more dilute smoke, dilution air can be added via a port in the intake line. The port is designed to allow adequate mixing of the dilution air and smoke before entering the chamber. Orifice flowmeters permit measurement of the inlet, exhaust and dilution air flow rates. To allow for rapid filling of the chamber, a variable speed exhaust fan pulls smoke through the chamber at flow rates up to 8 m³ per minute. Using the variable speed fan and inlet tips of diameters ranging from 1.5 to 10 cm, the inlet velocity can be matched with the stack velocity for isokinetic sampling. The smoke enters and exits the chamber through 10 cm diameter stainless steel duct work. After the chamber is filled and well mixed, two stainless steel butterfly valves, one on the inlet and one on the outlet, are simultaneously closed to capture a 1 m³ sample. A 100 liter piston which is located on top of the chamber allows the volume of the chamber to be reduced as samples of smoke are withdrawn from any of the 20 sampling ports. A pair of the sampling ports have been adapted for a

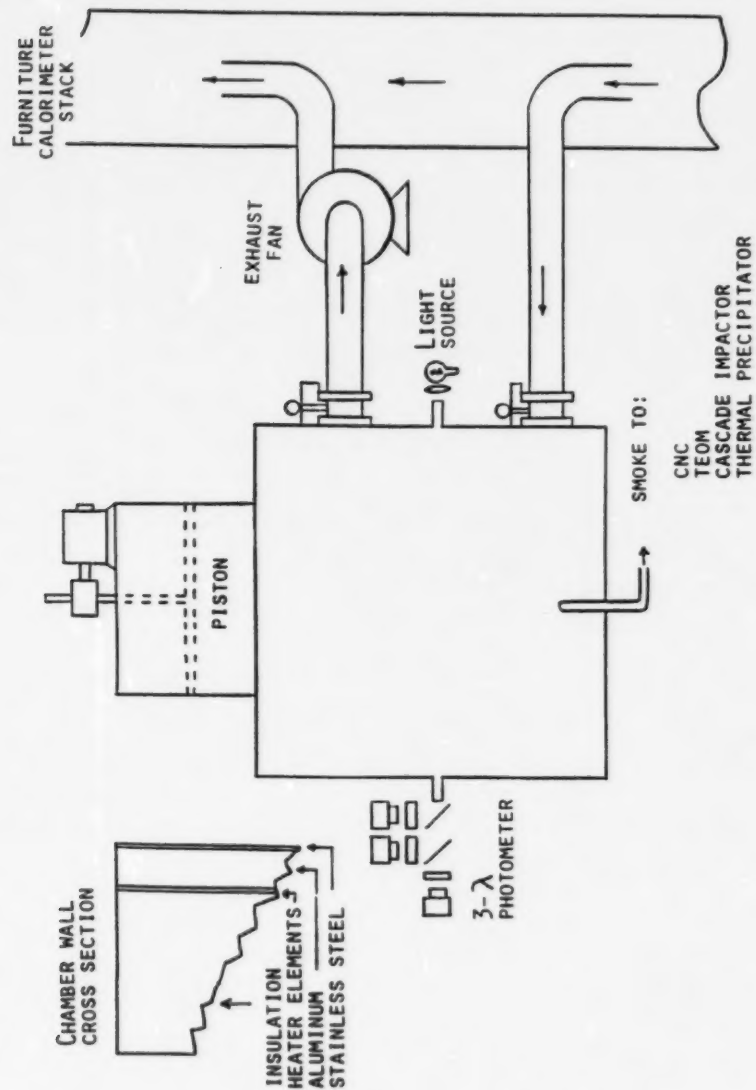


Figure 14. Smoke Aging and Dilution Chamber.
 (CNC - Condensation Nuclei Counter)
 (TEOM - Tapered Element Oscillating Microbalance)

three wavelength photometer for extinction measurements. Some of the other instruments which will be used with the chamber include the tapered element oscillating microbalance, a seven stage cascade impactor, a condensation nuclei counter and the transmission cell-reciprocal nephelometer.

For the preliminary work with crude oil fires, light extinction, mass concentration and size distribution data were collected with the photometer, microbalance and impactor. The photometer which is similar to Cashdollar's [8] design, consists of a white light source, two beam splitters, three interference filters and three photodiodes. Mounted on opposite walls of the chamber, the light source and the receiving optics are separated by pathlength of 1.1 meters. Measuring the amount of light extinction at 450, 630 and 1000 nm, the photometer allows calculation of the extinction coefficient at each wavelength. In order to calculate the amount of extinction per unit mass concentration of smoke, the mass concentration of the smoke in the chamber is determined with the Tapered Element Oscillating Microbalance (TEOM). Approximately two liters of smoke are necessary to make a mass concentration measurement.

While the photometer measures light extinction and the TEOM determines mass concentrations, a seven stage cascade impactor provides size distributions of the fresh smoke, as well as the aged smoke. The cascade impactor aerodynamically classifies the smoke aerosol by allowing the smoke to cascade through succeeding orifice stages with successively higher orifice velocities. The larger particles are inertially impacted on the early collection stages and successively smaller particles are inertially impacted on following stages. Particles smaller than $0.4\ \mu\text{m}$ are collected on a backup filter. The particles are classified into seven bins ranging from $0.4\ \mu\text{m}$ to $10\ \mu\text{m}$.

A preliminary series of experiments were performed to look at the effect of aging on smoke properties. Samples of crude oil smoke were collected and aged for up to 150 minutes, during which time mass concentration, size distribution and light extinction measurements were obtained. The mass concentration peaked at about $200\ \text{mg/m}^3$ just after the chamber was filled with smoke. Generally, the mass concentration decreased by a factor of about 2 over the 150 minute aging period due to settling given the inferred velocities. The TEOM measured the mass concentrations every 10 minutes throughout the aging experiment. As the crude oil smoke was aged for 90 minutes, the median aerodynamic diameter based on a mass weighting increased from about $0.8\ \mu\text{m}$ to about $1.1\ \mu\text{m}$ (Figure 15). The term aerodynamic diameter means that the particle settles with the same velocity as a unit sphere with this diameter. The $0.8\ \mu\text{m}$ and $1.1\ \mu\text{m}$ aerodynamic diameters correspond to settling velocities of $0.03\ \text{mm/s}$ and $0.06\ \text{mm/s}$, respectively. Aging the smoke for 150 minutes resulted in a mass median diameter of about $2.5\ \mu\text{m}$.

The specific extinction area, σ_s , at 450, 630 and 1000 nm did not change significantly over a 90 minute aging experiment (Figure 16). Three wavelength extinction data were collected every 10 minutes throughout the aging period. The mean value for σ_s were 5.1 (1000 nm), 8.0 (630 nm), and 9.7 (450 nm). In last year's study, we found σ_s equal about 10 based on laser transmittance ($\lambda=633\ \text{nm}$) through the stack for the steady burning phase. We obtained a value of about 8 based on data collected over the entire burn.

We are planning more studies utilizing the aging facility to include the determination of the agglomeration coefficient using the condensation nucleus counter, the settling velocity of the smoke, as well as the effect of aging on the size distribution and optical properties.

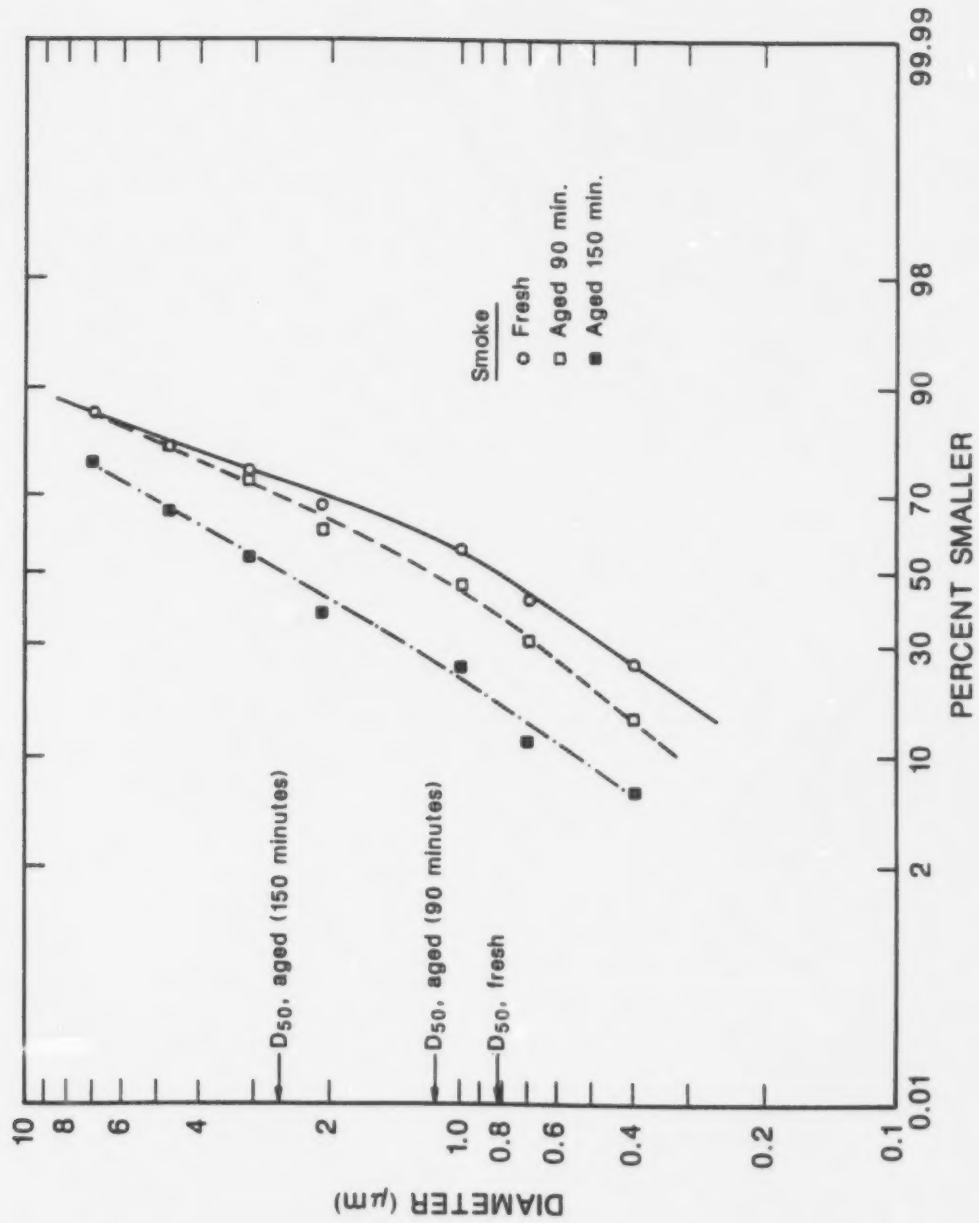


Figure 15. Effect of aging on mass distribution of crude oil smoke.
(Log - probability plot)

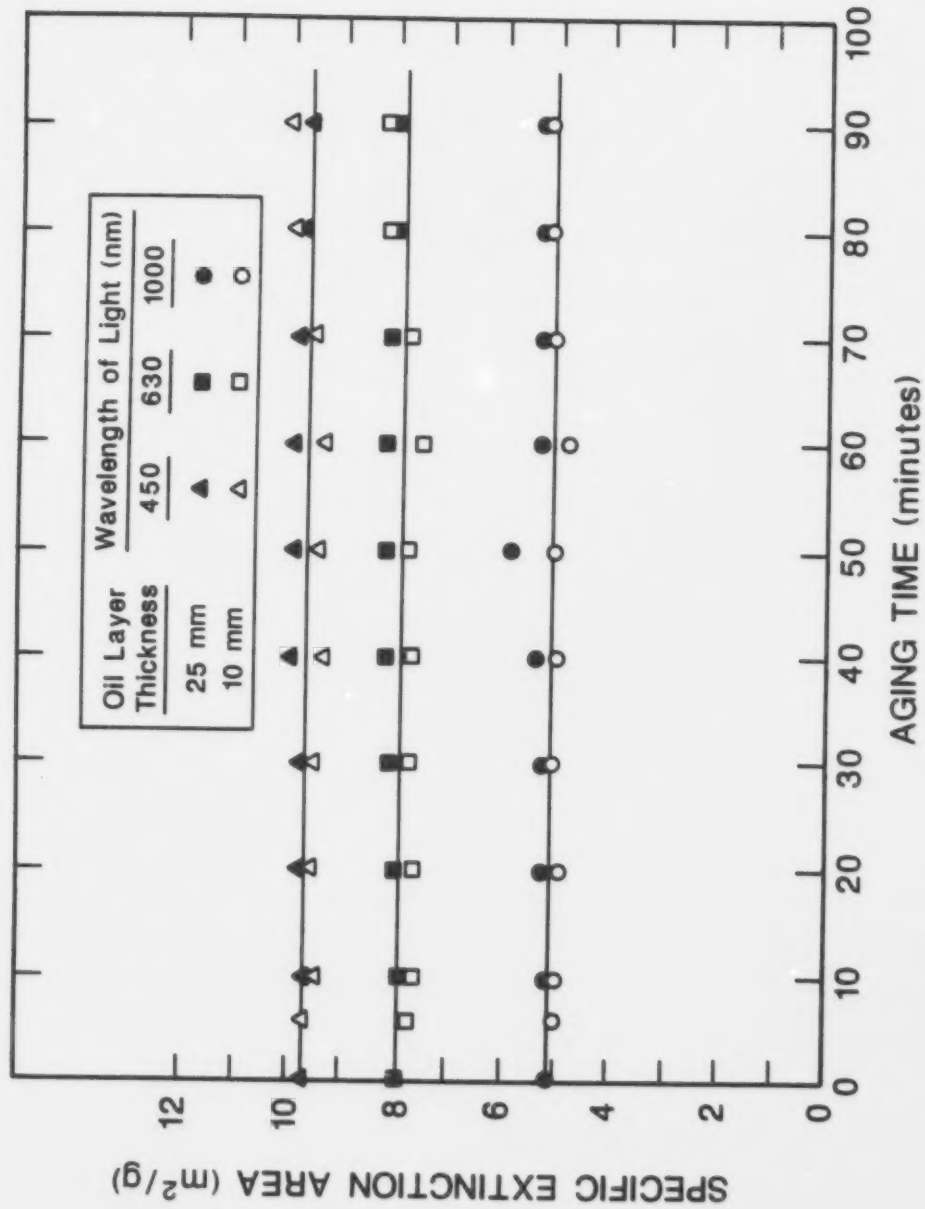


Figure 16. Effect of Aging on optical properties of crude oil smoke.

Discussion

The major focus of this study is the effect of oil layer thickness on the smoke emission and its chemical properties. We find that the smoke yield, ϵ , increases from 0.035 to about 0.080 as the layer thickness is increased from 2 mm to 10 mm. We also observe that for the 2 mm and 3 mm layer thicknesses about 65% of the mass loss takes place in the boilover mode, while for the 10 mm thickness only about 33% of the mass loss occurred during the boilover. We suspect that the high water vapor emission during the boilover phase is responsible for the decreased smoke emission. For a 10 mm burn, we observe a reduction in σ_f , which is proportional to ϵ , from a peak value of about 1.2 during the steady burning phase to a value of 0.2 - 0.4 during the boilover phase. This is another indication that the boilover is affecting the smoke production. In a follow on study, we plan to sample only the smoke produced during the boilover phase to better characterize the amount emitted and its properties.

In a review of the effect of water on combustion [9], Dryer indicates that the presence of water in residual water/oil emulsion can lower the particulate emission. The reduced flame temperature resulting from the higher heat capacity of water vapor compared to nitrogen is thought to be an important factor regarding soot emission. Schug *et al.* [10] have demonstrated that the reduction in the sooting tendency of an ethene laminar diffusion flame with added water vapor is primarily a thermal effect. Rao and Barden [11] report that the amount of soot leaving the flame decreases and that the peak flame temperature decreases with increasing water vapor concentration for laminar burning of diesel emulsion. In contrast, the peak flame temperature measured with a thermocouple for the 1.2 m diameter pool of Alberta Sweet crude oil increased by about 100 °C at boilover rather than decreasing as in the laminar flame studies [10,11]. However this boilover effect is not simply water vapor addition with everything else held fixed. The boilover phenomenon increases the fuel generation rate several fold and also appears to enhance the mixing of air and fuel droplets near the fuel surface. While we expect boilover to be important in reducing soot emission at realistic scale fires, field scale, and additional laboratory scale turbulent burning studies will be essential in understanding the scaling effects because of the complex coupling between boilover, fuel generation rate, mixing, and radiation feedback to the surface.

While the total smoke emission is significantly affected by the layer thickness, it appears from measurements made both at NBS and Environment Canada that both the total amount and the distribution of PAHs per gram of smoke is not greatly affected by the layer thickness. Of course, since less smoke is emitted per gram of fuel consumed, the yield of PAHs is lower for the smaller layer thicknesses. The total PAH emitted per gram of fuel consumed is on the order of a factor of two-three times less for the 2 mm layer compared to the 10 mm layer.

In this study we have collected both the vapor and particulate phase PAHs and find that a majority of the three ring PAH may be in the vapor phase. For a collection temperature of about 35° C, we find that 20 to 60% of anthracene is collected on the filter and 60 to 100% of fluoranthene is collected on the filter. These values are to be compared with 90% retention for anthracene and a 100% for fluoranthene reported by Longwell [12] for 40° C collection temperature. Clearly, there are effects other than the collection temperature controlling the fraction of PAH on the filter. We find that desorption can be significant and one also expects the mass concentration of the smoke to play an important role.

The PAH concentrations for the Alberta Sweet crude oil and the burn residue are very similar; in fact, it might be possible to use the PAH distribution in the burn residue to identify the crude oil that was burned. In the higher vapor pressure C_1 to C_4 alkanes and the mono-ring aromatics including benzene, toluene and xylenes, it has been reported by Evans *et al.* [13] that the residue is depleted relative to the crude oil. The PAH analysis at NBS indicated a high concentration of alkylphenanthrenes in the oil and residue but a very small concentration in the smoke. This indicates that very little unburned oil becomes deposited on the smoke. The Environment Canada data indicate a very low concentration of 4 and 5 ring PAHs. The analysis of PAH in the oils and residues was much more difficult than the smoke because of components in the oil interfering with the chromatographic separation of the PAH.

This may be the most complete and careful study regarding PAH emission from a fuel. This data should be useful as a first step in assessing the environmental impact of burning crude oil at sea. There is now a critical need for smoke data at the field scale for realistic oil layer thicknesses. The data at 0.6 and 1.2 m scale indicates a decrease in unburned oil residue and a decrease in smoke yield as the pool diameter increases. These trends may continue to field scale, but other combustion effects involving radiation that are significant only at field scale require testing to be performed at that scale.

Preliminary data obtained with the Aging/Dilution facility suggests that particle agglomeration leads to about a 30% increase in aerodynamic particle size over a 90 minute aging period. The actual smoke from a large fire would entrain air and be diluted so that 90 minutes of aging in the chamber could correspond to a day of aging in a smoke plume. This observed increase in particle size with aging does not seem to affect the specific extinction areas measured at 450, 630, and 1000 nm. This result is consistent with the idea proposed by Mulholland *et al.* [14] that for low density agglomerates made up of spheres much smaller than the wavelength of light the optical absorption per unit mass would be independent of agglomerate size. The aging/dilution facility will be used to measure the settling velocity of the agglomerates and the settling rate of a cloud of particles. We expect that cloud settling to be the controlling mechanism for particle deposition as discussed in the next section.

Particulate Settling Analysis

The purpose of this section is to develop a method for solving the equations which govern the evolution of a smoke particle plume; from the point at which it is injected into the atmosphere until it is finally deposited on the ground. The mathematical model on which the analysis is based is a special case of that developed by the authors in the proceeding Technical Seminar in this series [1] and will not be re-derived here. The principal assumptions underlying the model are:

- 1) The fire generating the smoke and hot gases is burning steadily.
- 2) The injection altitude and particle mass flux associated with the fire are known.
- 3) The gas temperature in the buoyant plume equilibrates with the atmosphere before any significant particle settling begins.

- 4) The ambient wind speed is much larger than the velocities induced by the negatively buoyant smoke particle plume.
- 5) Individual particle settling velocities are much smaller than the collective effects represented by the smoke particle plume.
- 6) The stratification of the atmosphere plays no role in the settling process.

The last assumption limits the injection altitude for which the analysis is valid to at most one kilometer. The determination of the injection altitude itself is not part of this analysis, although it does fit within the framework of the mathematical model developed earlier. The goal of the present study is the ability to predict the downwind deposition pattern of the smoke particulate on the ground. The controlling parameters are the injection altitude and initial cross-section area of the plume, the particulate mass flux, and the ambient wind velocity.

To proceed, we introduce a cartesian coordinate system X, Y, Z as shown in figure 17. The variable X increases in the direction of the ambient wind, Z is directed vertically upward, and Y is horizontal coordinate perpendicular to the other two. Let U, V and W be the air velocity components in the X, Y and Z directions respectively. In this model U is the ambient wind speed and is presumed known. The smoke particulate is described in terms of a mass density ρ_p , mass flux M , and initial cross sectional area L^2 . The initial injection altitude H is defined as the distance from the level ground to the initial center of mass of the plume. The atmosphere is characterized by an ambient density ρ_0 and the magnitude of the gravitational acceleration is g . Dimensionless coordinates, velocity components, and smoke density can be introduced in terms of these parameters as follows:

$$\begin{aligned} (Y, Z) &= L (y, z) \\ X &= (LU)^{3/2} / (gM/\rho_0)^{1/2} t \\ (V, W) &= (gM/(\rho_0 UL))^{1/2} (v, w) \\ \rho_p &= M/(UL^2) \rho \end{aligned} \quad (1)$$

The dimensionless horizontal (v) and vertical (w) velocities induced by the settling process, as well as the dimensionless smoke particulate density ρ are functions of the reduced transverse horizontal coordinate (y), vertical coordinate (z), and downwind coordinate (t). This nomenclature is introduced because the mathematical model of this three-dimensional steady state process is equivalent to a two dimensional time dependent process viewed in a cross-sectional plane moving downwind at the ambient wind speed U . Thus, the smoke distribution in the upwind plane $X=X_1$ in figure 17 evolves over a time interval defined by the second of eqs. (1) into the distribution at the downwind station $X=X_2$ in the figure.

The equations describing the evolution process can be written in the form:

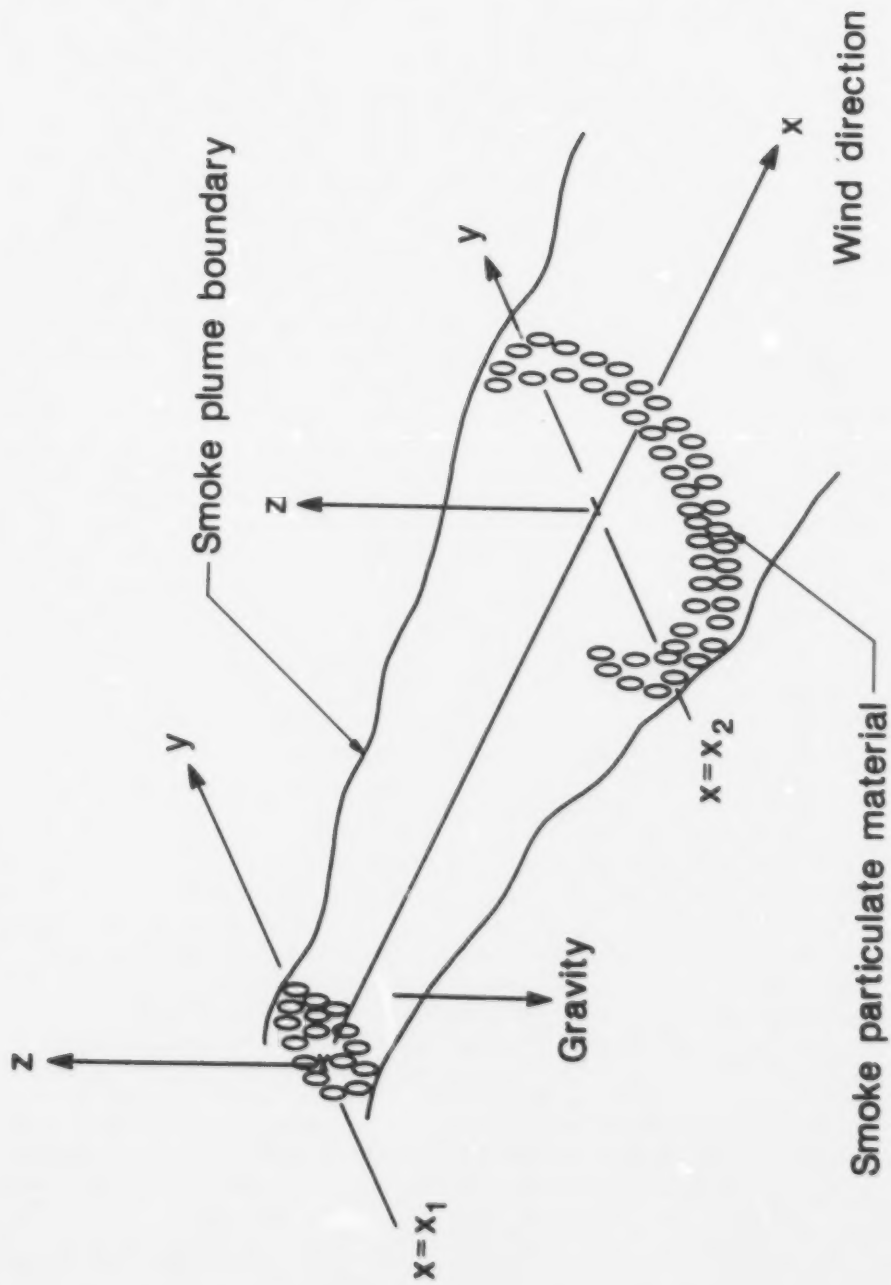


Figure 17. Schematic showing downwind evolution of smoke plume.

$$\begin{aligned}
\frac{\partial \rho}{\partial t} + v \frac{\partial \rho}{\partial y} + w \frac{\partial \rho}{\partial z} &= 0 \\
\frac{\partial \omega}{\partial t} + v \frac{\partial \omega}{\partial y} + w \frac{\partial \omega}{\partial z} &= - \frac{\partial \rho}{\partial y} \\
\frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} &= 0 \\
\frac{\partial w}{\partial y} - \frac{\partial v}{\partial z} &= \omega
\end{aligned}
\tag{2}$$

The first two of equations (2) govern the evolution of the particle density and the windward component of the vorticity ω , while the last two determine the transverse velocity field at each instant in terms of ω . Equations (2) must be supplemented by initial and boundary conditions. Upwind at the injection point $t=0$:

$$\rho(y, z, 0) = f(y, z) \tag{3}$$

$$v(y, z, 0) = w(y, z, 0) = 0$$

The initial particulate density distribution $f(y, z)$ is presumed known. Since the mass flux M is specified, $f(y, z)$ is subject to the constraint:

$$\iint dy dz f(y, z) = 1 \tag{4}$$

The ground is defined by the plane $z = -H/L$ in the present coordinate system. Since the velocities cannot penetrate the ground anywhere, the vertical velocity w must satisfy the boundary condition

$$w(y, -H/L, t) = 0 \tag{5}$$

Finally, both components of the settling induced velocities must vanish sufficiently far from the plume

$$\lim_{y, z \rightarrow \infty} (v, w) = 0 \tag{6}$$

Note that the system of equations (2)-(6), which constitute the mathematical model, depends only on the initial density distribution $f(y, z)$ and injection altitude parameter H/L . We wish to follow the particle density downwind until most of the smoke is within some specified small distance of the ground, at which point it can be regarded as having settled out of the system. Since the primary interest is in the location of the particulate matter, the numerical method must focus on the Lagrangian coordinates of the smoke, rather than the general flow field. To this end, it is convenient to replace the continuous model of the smoke density by discrete clumps of matter s shown in figure 18. Each clump of matter carries a specific particulate mass flux and a vorticity which changes with time. The second of equations (2) shows that the vorticity is induced by horizontal density gradients, with positive gradients inducing negative vorticity as illustrated in figure 18.

The mathematical basis for this discretization is the introduction of a

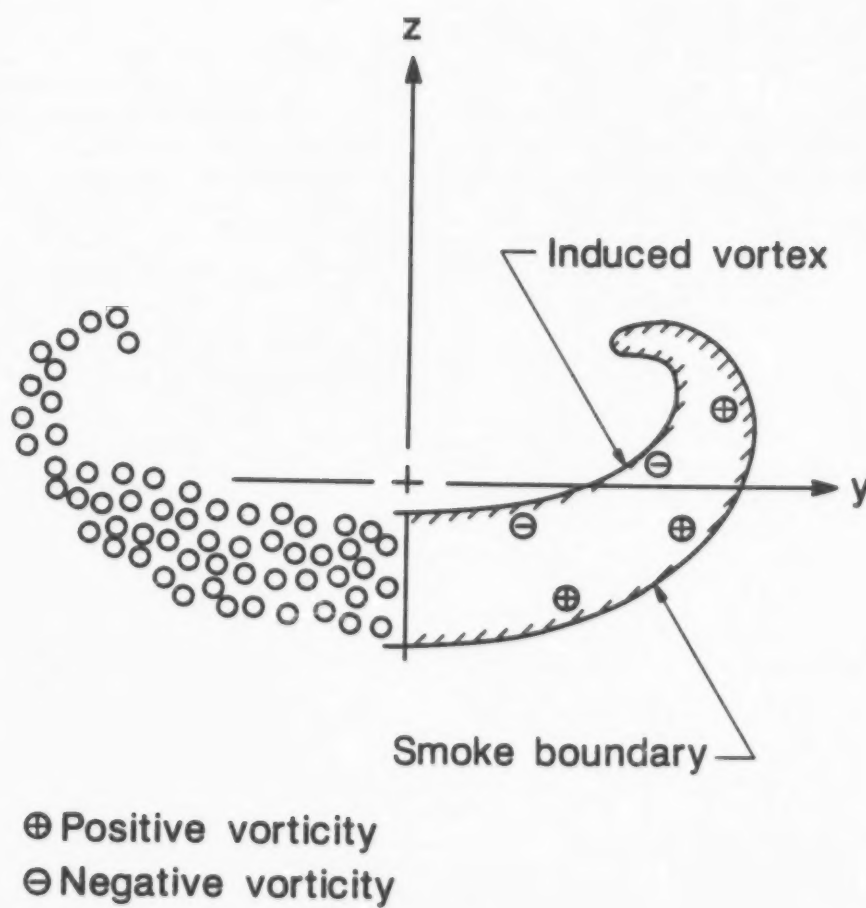


Figure 18. Discretization of smoke into vorticity containing clumps. Horizontal density gradients induced vorticity.

Lagrangian coordinate system. Each clump of matter is characterized by its initial coordinates as follows:

$$\text{at } t = 0; y = \eta; z = \zeta \quad (7)$$

Then, the coordinates y, z are calculated as functions of time as solutions of the differential equations

$$\frac{\partial y}{\partial t} = v(y, z, t) \quad \frac{\partial z}{\partial t} = w(y, z, t) \quad (8)$$

There is one pair of such equations for each clump; i.e. for each value of η, ζ . To generate the velocity fields, the evolution equations for the vorticity and density, the first two of eqs. (2), need to be rewritten in terms of the new coordinate system. The appropriate formulae are:

$$\rho = f(\eta, \zeta) \quad (9)$$

$$\frac{\partial \omega}{\partial t} = S \frac{\partial f}{\partial \zeta} - T \frac{\partial f}{\partial \eta}$$

Note that the quantity $f(\eta, \zeta)$ is the initial upwind density distribution, and that the density does not change in this system of coordinates. This is the mathematical statement of the fact that the mass flux associated with each clump is always the same as the clump progresses downwind.

The generation of the vorticity fields involves four coordinate gradients which describe the mixing and stretching of the fluid by the vortices. These quantities, denoted Q, R, S , and T are defined as follows:

$$\begin{aligned} \frac{\partial y}{\partial \eta} &= Q(\eta, \zeta, t) & \frac{\partial y}{\partial \zeta} &= R(\eta, \zeta, t) \\ \frac{\partial z}{\partial \eta} &= S(\eta, \zeta, t) & \frac{\partial z}{\partial \zeta} &= T(\eta, \zeta, t) \end{aligned} \quad (10)$$

To preserve the intent of this method, it is important not to actually compute any spatial derivatives numerically. To avoid this, we note that analytical recipes for $v(y, z, t)$ and $w(y, z, t)$ can be generated and that these recipes can be exactly differentiated. The procedure for generating these recipes will be indicated briefly below. Given the existence of such expressions, however, it is easy to generate evolution equations for Q, R, S , and T . The necessary equations are:

$$\begin{aligned} \frac{\partial Q}{\partial t} &= Q \frac{\partial v}{\partial y} + S \frac{\partial v}{\partial z} \\ \frac{\partial R}{\partial t} &= R \frac{\partial v}{\partial y} + T \frac{\partial v}{\partial z} \\ \frac{\partial S}{\partial t} &= Q \frac{\partial w}{\partial y} + S \frac{\partial w}{\partial z} \\ \frac{\partial T}{\partial t} &= R \frac{\partial w}{\partial y} + T \frac{\partial w}{\partial z} \end{aligned} \quad (11)$$

Equations (8), (9), and (11) constitute a set of seven ordinary differential equations and one algebraic statement that must be solved to describe the

evolution of each clump. They are equivalent to solving equations (2) everywhere in space. Obviously, any method which attempts to solve the equations everywhere is going to yield a much cruder approximation to the quantities of interest than one which concentrates attention directly on the desired information. Thus, it is worthwhile to expend this much effort on tracking the fate of a single clump of particulate matter, if no resources have to be devoted to calculating quantities outside the smoke cloud.

The final piece of information required to implement this method is the explicit representation of the velocities in terms of the coordinates y, z . To this end, it is convenient to introduce a stream function $\Psi(y, z, t)$ that satisfies the third of eqs. (2) identically.

$$\frac{\partial \Psi}{\partial z} = v; \quad \frac{\partial \Psi}{\partial y} = -w \quad (12)$$

Substitution of eqs. (12) into the last of eqs. (2) yields a Poisson equation for Ψ in terms of ω . The solution can be expressed in terms of a Greens function $G(y, z, y_0, z_0)$ as:

$$\begin{aligned} \Psi &= \iint dy_0 dz_0 G(y, z, y_0, z_0) \omega(y_0, z_0, t) \\ G &= -\frac{1}{2\pi} \left\{ \log(r_+) - \log(r_-) - \log(rI_-) + \log(rI_+) \right\} \\ (r_+)^2 &= (y-y_0)^2 + (z-z_0)^2 \\ (r_-)^2 &= (y+y_0)^2 + (z-z_0)^2 \\ (rI_-)^2 &= (y-y_0)^2 + (z + [2(H/L) + z_0])^2 \\ (rI_+)^2 &= (y+y_0)^2 + (z + [2(H/L) + z_0])^2 \end{aligned} \quad (13)$$

Physically, the Greens function represents the flow induced by the vortex pair associated with two clumps as shown in figure 19a. The signs of the vortices are such that the direction of the swirling motion, as indicated by the arrows, induces a downward flow. This accounts for the first two terms in the expression for G . The last two terms account for the image vortices shown in figure 19b generated by the presence of the ground. They induce the swirling motions shown by the arrows which tend to push the clumps of particulate outward as they near the ground.

The numerical simulation will require the simultaneous tracking of a few thousand clumps of material to adequately represent the turbulent mixing generated by the settling process. Numerical methods of this kind to simulate processes quite analogous to the one of interest here have been pioneered by Ghoniem [15], who has demonstrated their ability to predict overall characteristics of turbulent flows. The approach taken here is more specialized than his, but will hopefully yield more accurate results for the particular problem with which we are concerned.

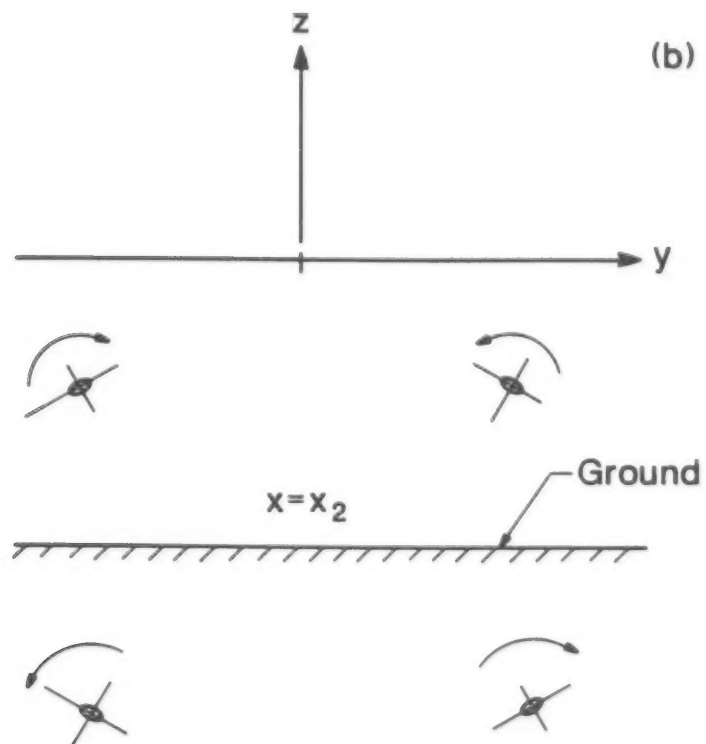
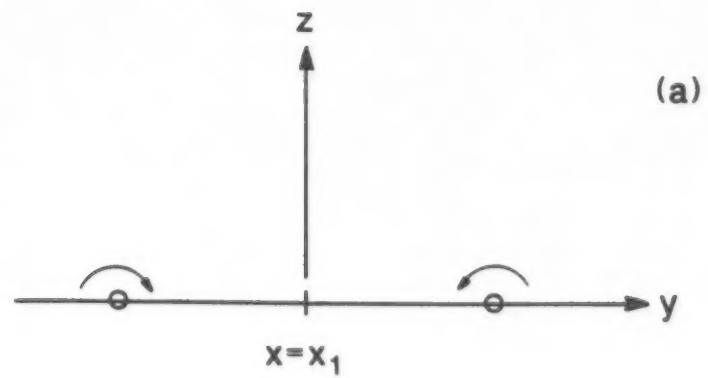


Figure 19. Fluid motion induced by vortices is indicated by direction of arrows. Ground effect is represented by image vortices.

CONCLUSIONS

Increasing oil surface temperature and smoke production during the burning of crude oil pool fire are evidence that lower boiling temperature fractions are consumed preferentially during the early part of the burn.

The smoke production during boiling of the supporting water layer is reduced by up to a factor of five when compared to that with no boiling. The smoke yield decreases by more than a factor of two as the oil layer thickness is decreased from 10 mm to 2 mm. The smaller yield for the thin oil layer results from boiling in the water layer occurring over most of the burn.

The total PAH contained in the oil residue and the smoke and vapors produced by combustion is less than that contained in the oil that was burned. The crude oil and the residue which is left on the water have the same relative concentration of the various PAH compounds measured on a per unit mass of original oil basis. However, the concentration of PAHs with 5 or more rings, which includes benzo[a]pyrene, is 10 to 20 times greater in the smoke compared to the fuel. While about 90% of the PAHs for the oil and residue have three rings, the PAH content of the smoke/vapor is equally divided among three rings, four rings, and 5 or more rings.

As the PAH concentrations for the Alberta Sweet crude oil and the burn residue were found to be very similar, it might be possible to use the PAH distribution in the burn residue to identify the crude oil that was burned.

Particle agglomeration for Alberta Sweet crude oil smoke measured in the aging/dilution chamber over 90 minutes (corresponding to approximately one day in an actual fire plume) leads to a 30% increase in aerodynamic particle size.

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RECOVERY OF A NOVA SCOTIAN SALTMARSH DURING TWO GROWING
SEASONS FOLLOWING EXPERIMENTAL SPILLS OF CRUDE OIL AND THE
DISPERSANT COREXIT 9527

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ABSTRACT

This study documented the effects of experimental applications of Alberta sweet blend crude oil on the creek edge, midmarsh and high marsh zones of a Nova Scotia salt marsh over the course of two growing seasons. It also investigated the impact of the dispersant Corexit 9527 on the creek edge vegetation zone. The effects of the oil and dispersant applications were monitored using a number of parameters, including; plant height growth, stem density, biomass, and species cover. These data revealed that there was considerable variation in the sensitivity of the three vegetation zones to the oil treatment. The oil treatment had little effect on the creek edge zone (dominated by tall Spartina alterniflora) during the 1986 growing season and no residual effects were noted in 1987. The midmarsh zone (dominated by dwarf S. alterniflora) by contrast was severely impacted by the oil in 1986 and displayed relatively little recovery during the 1987 growing season. The large differences in toxicity between the creek edge and midmarsh zones appeared to be related to the inability of S. alterniflora growing in the physiologically stressful mid marsh zone to tolerate the additional stress of oil toxicity. Oil impacts in the high marsh zone (dominated by S. patens) were intermediate between those of the creek edge and midmarsh zones. Significant negative impacts were noted for most of the study parameters in 1986, however, the heavy mortality observed in the midmarsh zone was not found there. Data from the 1987 growing season revealed relatively little recovery. The creek edge dispersant treatment had severe negative effects on this community in 1986, however, rapid recovery was observed in 1987.

Species cover data for 1986 and 1987 revealed similar successional trends for the three vegetation zones following the application of oil or dispersant. Annual species, the most abundant of which were Salicornia europaea and Suaeda maritima, increased in abundance in plots where interspecific competition had been reduced by oil or dispersant induced mortality of Spartina. Based on current rates of recovery, the creek edge zone recovered from oiling within one year of treatment and will probably recover from the dispersant treatment within two years. The high marsh zone will probably require three to four years for full recovery, while the midmarsh zone will probably require at least five years.

INTRODUCTION

Salt marshes are highly productive ecosystems which are of great ecological and economic importance. Salt marshes fix large quantities of carbon, a large proportion of which is exported to estuarine and coastal waters where it fuels marine food webs. Many species of invertebrates, fish and birds utilize salt marshes as feeding, breeding and resting areas. Most of the salt marshes along the Atlantic coast of North America are dominated by the salt marsh cord grass (Spartina alterniflora Loisel). This species is tolerant of high salinity and anoxic conditions in the sediment, yet is capable of very high rates of primary productivity.

Salt marshes are highly susceptible to oil spills since they are regularly inundated by seawater and have low self cleaning potential as a result of the low energy nature of the areas in which they develop. Much variation has been found in the sensitivity of salt marshes to oil spills. Oil toxicity depends on a number of factors including type of oil, the degree of oil weathering, amount spilled, frequency of multiple spill events, time of the year in which the spill occurred, the types of organisms exposed to the oil and the amount of stress experienced by these organisms prior to the oil spill. These factors make it difficult to implement proper mitigative measures when salt marshes are threatened by oil spills. This situation is further complicated by the fact that most salt marsh clean up techniques are ineffective or cause as much if not more damage than the oil (Vandermeulen and Jotcham, 1986). No intervention may be a valid option provided the impact of the oil spill is less than that of the potential clean up option. Evaluation of this option requires the development of oil spill impact studies in a variety of salt marsh communities using different types and amounts of oil applied at different times of the year and monitored over a number of

years. This is beyond the scope of most investigations, however, useful information can be derived from a variety of smaller studies.

The dispersal of incoming slicks offers a means of reducing the amount of oil entering the marsh. Generally the use of dispersants in shallow near shore waters is not recommended but may be attempted if it will reduce the amount of oil stranding in the marsh (API, 1985). Near-shore applications of dispersant increase the likelihood of dispersant contamination of salt marsh vegetation. Few studies have investigated the impacts of dispersants on salt marsh plant communities (Baker et al, 1984; Delaune et al., 1984 and Smith et al, 1984). These studies have demonstrated that the phytotoxicity of various dispersant formulations varies considerably. It is therefore important to document the toxicity of a variety of dispersants in order to determine which may be safely used in close proximity to salt marsh vegetation.

In this study, the impacts of Alberta sweet blend crude oil and the dispersant Corexit 9527 were studied in a Nova Scotia salt marsh over the course of two growing seasons. The impacts of experimental crude oil spills were investigated in creek edge, midmarsh and high marsh vegetation zones while dispersant impacts were studied only in the creek edge zone. This is a continuation of a study initiated in 1986 (Lane et al., 1987) and presents data collected during both the 1986 and 1987 growing seasons following the oil and dispersant applications in 1986.

MATERIALS AND METHODS

Description of Study Site

The field study site was located at Conrods Beach on Petpeswick Inlet (44°42'N, 63°11'W). This marsh has developed behind a barrier dune system, and is drained by a single channel which penetrates the dune system. The vegetation of the salt marsh was composed of three distinct zones, which will be referred to as creek edge, midmarsh, and high marsh zones.

The creek edge zone was dominated by a lush growth of Spartina alterniflora. Small quantities of Salicornia europaea, Plantago juncooides, Suaeda maritima, and Atriplex patula were also present in this zone. The distribution of the creek edge zone was usually restricted to within two metres of drainage channels in the marsh. The lush growth of Spartina alterniflora was attributable to the relatively well drained sediments of this zone.

The midmarsh zone was dominated by short Spartina alterniflora, with lower abundances of Spartina patens, Salicornia europaea, Suaeda maritima, Triglochin elata, Limonium nashii, and Plantago juncooides.

This was the most extensive of the three zones in the Conrods Beach salt marsh and was generally found in poorly drained areas in the marsh interior. The stunted growth of Spartina alterniflora in the midmarsh zone is generally associated with extremely low redox potential of the sediments and high salinity of the interstitial water of the sediments of this zone.

Spartina patens was the dominant species of the high marsh zone. Small quantities of Spartina alterniflora, Salicornia europaea, Triglochin elata, Suaeda maritima, and Glaux maritima were also found in association with S. patens. The high marsh zone was located on slightly elevated, better drained and aerated soils of the marsh.

Experimental Design

A total of twenty-one 0.4m x 4.0 m (2m²) plots were established at random locations in the salt marsh. Nine plots were positioned in the creek edge zone, with three replicate plots assigned to each of three treatments (control, oil and dispersant). In the midmarsh and high marsh zones, only control and oil treatments were assigned for a total of six plots per zone. Each plot was separated from other plots by a 10 m buffer zone to prevent or reduce cross contamination by either oil or dispersant from other plots. Each quadrat was surrounded by a wall of oil sorbent material to prevent the escape of oil from the quadrat. Quadrats were also covered with garden netting to exclude wildlife. Field measurements commenced on May 9 (day 1) and treatments were applied on July 7 (day 60) in 1986.

Oil and Dispersant Applications

Alberta sweet blend crude oil, weathered by evaporation and stirring for 24 hours to 15-25% loss by weight, was used for all experiments. In the field experiments, 2.25 liters of weathered oil per plot were applied from a back-pack sprayer approximately two hours after the onset of the ebb period yielding a nominal 0.5 mm oil slick. The tide did not rise high enough to cover the marsh surface with water on the day of treatment applications, therefore, each plot was sprayed with seawater prior to treatment. The oil spray application was done so that the spray was held near the marsh sediment surface, at about half of the mean plant height; thereby, simulating contamination by a surface oil slick.

For the dispersant treatment, ethylene glycol-based Corexit 9527 was mixed with water in a ratio of 1 part dispersant to 10 parts seawater. A total of 2.25 liters of the dispersant/seawater mixture was applied to each plot from a back-pack sprayer. Application differed from that of the oil application, in that the dispersant spray was directed at the vegetation from 50 cm above the sediment

surface and only the creek eddge zone plots were treated. This application was intended to mimic a near shore application of dispersant on an incoming tide.

Vascular Plant Parameters

Plant Height Within each plot, 40 Spartina shoots were systematically selected at 10 cm intervals and their heights were measured. Plant height was measured as the distance from the tallest point of the plant to ground level. Measurements were taken on eight occasions during the growing season in 1986 and on five occasions during the 1987 growing season.

Stem Density Within each plot, 12 miniquadrats were systematically positioned at 30 cm intervals. In Spartina alterniflora dominated marsh zones (creek edge and midmarsh zones), 0.01m² quadrats were used while in the S. patens dominated zone (high marsh zone), 0.006m² quadrats were used. All shoots in each quadrat and all flowering shoots in each plot were counted and means and standard deviations were calculated for each treatment in each vegetation zone on each sampling date. Measurements were taken on four occasions during the 1986 growing season and on five occasions during the 1987 growing season.

Biomass Biomass harvesting was conducted in the first week of September in both 1986 and 1987. A 0.09m² quadrat was systematically positioned in one end of each plot and all above ground living biomass in the quadrat was harvested, sorted by species, dried at 80° C in a convection oven and weighed on an analytical balance. Mean above-ground standing crops for living plants, were calculated for each treatment in each vegetation zone for each year.

Species Cover Percent cover for each species of vascular plant was estimated in each plot. Cover values were estimated relative to soil surface area rather than to other species in the quadrat; therefore, total cover could be higher than 100% when species overlapped. Mean cover values were calculated for each species in each treatment in all vegetation zones for three sampling dates in 1986 and five sampling dates in 1987.

Statistical Analysis

Statistical analyses were conducted on plant height, stem density, above ground biomass and cover. In all cases, both 1986 and 1987 data were analysed. Transformations as determined by tests for

normality and homoscedasticity in 1986 were continued. Data analysis was conducted using the SPSS/PC+ V2.0 statistical package (Norusis, 1988a, 1988b). Graphs were produced with SPSS/U.C.+ Graphics (SPSS Inc., 1986).

Preliminary analysis consisted of both general descriptive statistics and analysis of variance to test whether replication was a factor. Subsequent analysis investigated the effects of treatments and time (year, and where appropriate, visit). The principle investigative technique was analysis of variance. The number of levels and the interactions tested varied with the particular data set.

Height data was transformed as follows:

$$y = \ln ((x/14) + 1).$$

where 14 was the overall median height for the 1986 data.

Density was also ln transformed:

$$y = \ln (x + 1).$$

Square root transformations were used on both cover and biomass data.

Cover data for the creek edge, midmarsh, and high marsh were entered into discriminant analyses. The results of 4 estimates for each plot on each sampling date were incorporated. The estimates were divided into groups according to treatment. All cover estimates from the first sampling date in 1986 were coded as controls since they preceded treatment applications. Separate ordinations were conducted including and excluding standing dead biomass.

RESULTS AND DISCUSSION

Plant Height

In the creek edge zone in 1986, significant reductions in plant height were noted on all post treatment days for dispersant treated plots (Figure 1 ($p < 0.001$, ANOVA)). Plant heights in dispersant treated plots increased substantially between days 102 and 123. This trend was probably caused by selective mortality of short plants which would increase mean plant height, although growth rates of surviving plants probably did not increase. Short plants would be at a disadvantage in competition for light and would, therefore, suffer more stress than the dominant plants resulting in higher mortality rates. The oil treatment had relatively little impact on plant height

Creek Edge

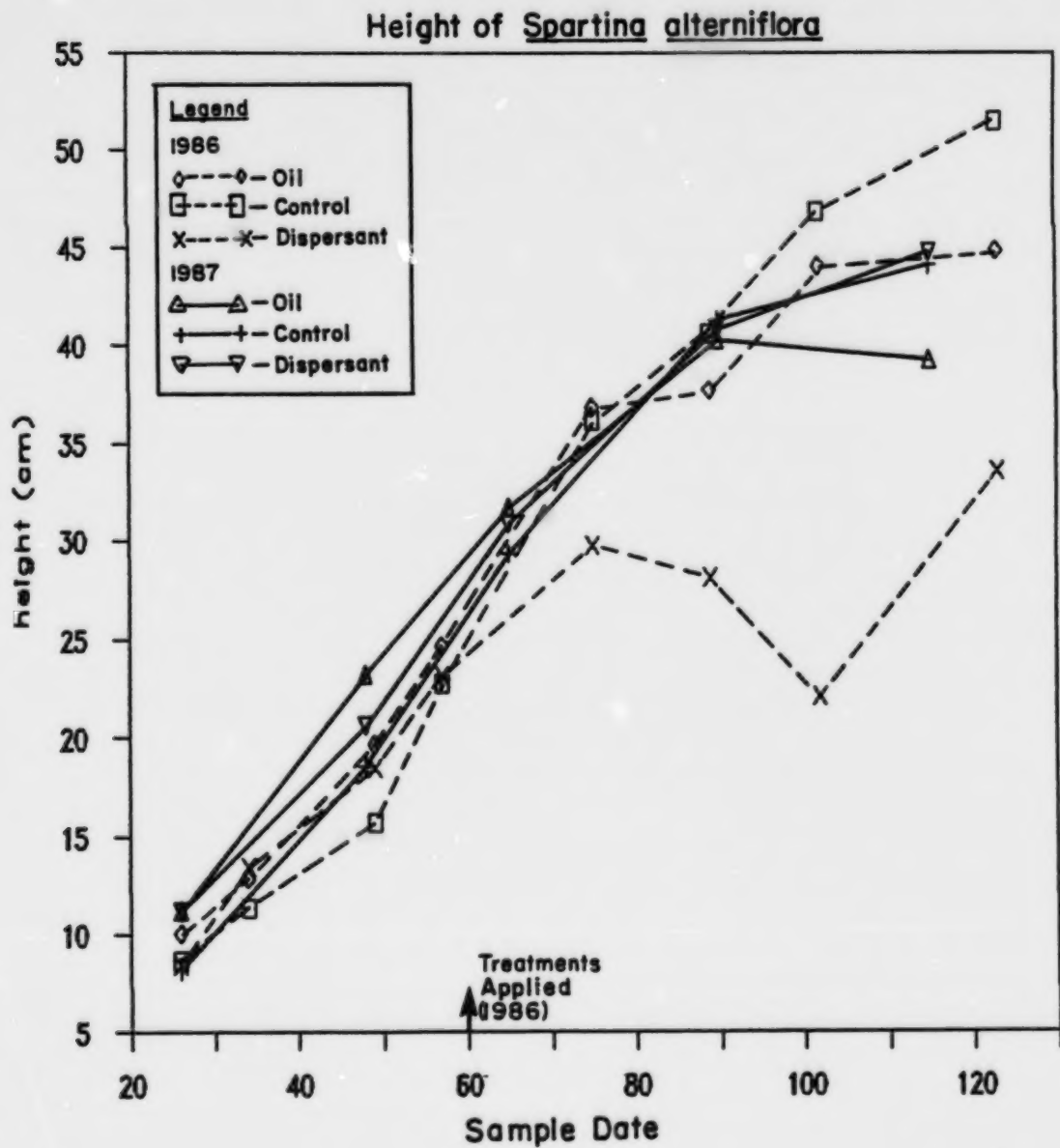


Figure 1. Plot of mean Spartina alterniflora height for the creek edge zone versus time.

in 1986, although oiled plants were significantly shorter than controls on days 89 ($p=0.043$, ANOVA) and 123 ($p=0.034$, ANOVA).

In 1987, there was little or no evidence of oil or dispersant impacts on height growth. Early in the growing season (days 26 and 48), oil and dispersant treated plants were slightly, although significantly, taller than control plants ($p<0.001$, $p=0.021$, ANOVA). This may be attributable to reductions in stem density associated with these treatments which would reduce competition and allow more rapid growth early in the growing season. No significant reductions in plant height were noted for any of the treatments later in the growing season with the exception of oiled plants on the last sampling date (day 115) ($p=0.034$, ANOVA).

These data suggest that there was a rapid recovery of plant height growth associated with the dispersant treatment. This is not unexpected since the water miscible dispersant would be rapidly dissipated by tidal action. Data for oiled plots indicated little change in height growth between 1986 and 1987. This suggests that the oil treatment had little if any short term or long term effects on height growth.

In the midmarsh zone in 1986, oil did not significantly reduce plant height growth (Figure 2). This was unexpected since heavy mortality was noted in oiled plots. High Mortality of small plants may have maintained mean plant height at an artificially high level during this period. This is supported by the fact that plant heights in oiled plots were significantly shorter than controls throughout 1987. It is difficult to determine whether there was any recovery of plant growth between 1986 and 1987 since trends for 1986 were masked by selective mortality of small plants making direct comparisons impossible. Data for 1987, however, indicate that plant height growth was still significantly affected by the oil treatment.

The larger reductions in Spartina alterniflora height in oiled midmarsh plots relative to similarly treated S. alterniflora in the creek edge zone were probably attributable to low sediment oxidation status (Eh) in the midmarsh zone, making it a more hostile environment for plants. (Howes et al., 1986) Low oxygen concentrations lead to decreased ability to take up nitrogen from the sediment (Morris and Dacey, 1984), increased root respiration rates (Mendelssohn et al., 1981) and increased production of hydrogen sulfide which is toxic to root metabolism (Allam and Hollis, 1972). Untreated S. alterniflora growing in the midmarsh zone were shorter than creek edge plants, indicating the stressful nature of the midmarsh zone. The additional stress of oil toxicity was enough to alter the carbon balance of the midmarsh plants (i.e. increased respiration decreased photosynthesis) to the point where height growth was slowed. In the creek edge zone

Mid Marsh

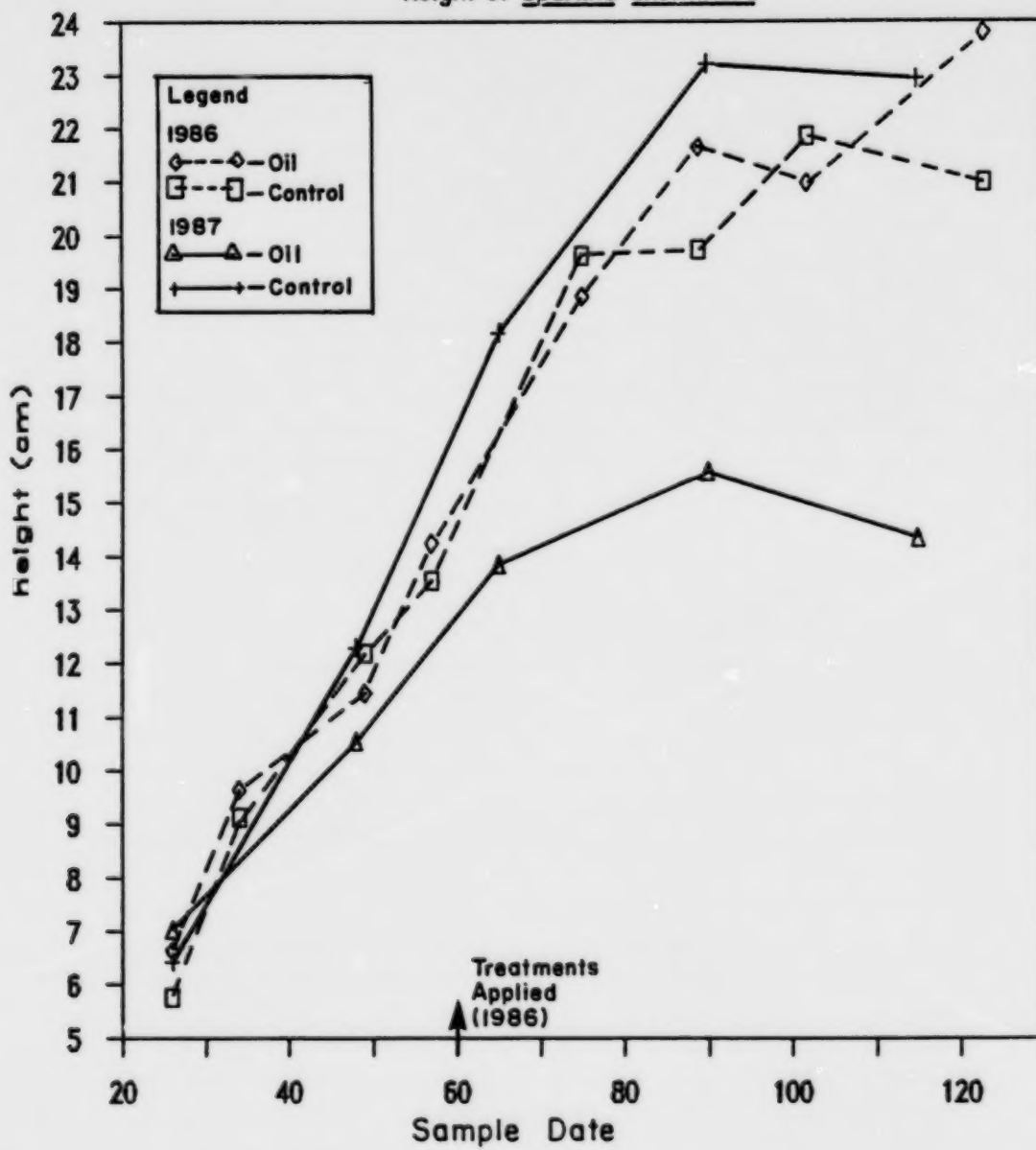
Height of *Spartina alterniflora*

Figure 2: Plot of mean *Spartina alterniflora* height for the midmarsh zone versus time.

the oil would alter the carbon balance in the same way, however, activities such as flowering which are relatively unimportant to rhizomatous plants such as Spartina would be sacrificed rather than height growth.

In the high marsh zone in 1986 (Figure 3), height growth of Spartina patens in oiled plots was significantly lower than the heights of control plants after treatment applications ($p < 0.001$, ANOVA). Height growth in 1987 was very similar to that noted in 1986 and was significantly lower than control heights from day 67 to the end of the sampling period ($p < 0.001$, ANOVA). These data suggest that there was virtually no recovery of height growth in the high marsh zone one year after the oil treatment. On the first sampling date in 1987 (Day 26), oiled plants were significantly taller than control plants. This trend was observed in all vegetation zones although it was significant only in the creek edge and high marsh zones. Reductions in stem density associated with the oil treatments may have reduced competition allowing more rapid growth early in the growing season.

Stem Density

In 1986, the oil treatment was associated with significant reductions in Spartina alterniflora stem density in the creek edge zone on all sampling dates following treatment application (Figure 4). On all sampling dates in 1987, however, oiled plots had higher stem densities than control plots. These differences were not statistically significant. This situation appeared to be attributable more to reductions in control stem density rather than to substantial improvements in oiled plot stem density. Nevertheless, the data does indicate a recovery of stem density in oiled plots. No clear reasons for reductions in control stem density were evident. Small reductions in stem density were also noted in all high marsh control quadrats and two out of three midmarsh control quadrats. Trampling damage to the periphery of the quadrats may have stressed plants within the quadrats resulting in reduced stem density or yearly variations in growing conditions might also be responsible. Summer rainfall was heavy in 1986 and extremely light in 1987. Drought conditions might be expected to increase osmotic stress in salt marsh plants resulting in stem density reductions.

The stem density of dispersant treated plots was significantly lower than control plots on all sampling dates in 1986 including pretreatment dates ($p < 0.001$, ANOVA). This indicated that control and dispersant treated plots were not directly comparable. Determination of dispersant impacts, therefore, was best determined by comparing data from 1986 and 1987 for the dispersant treated plots and comparing

High Marsh

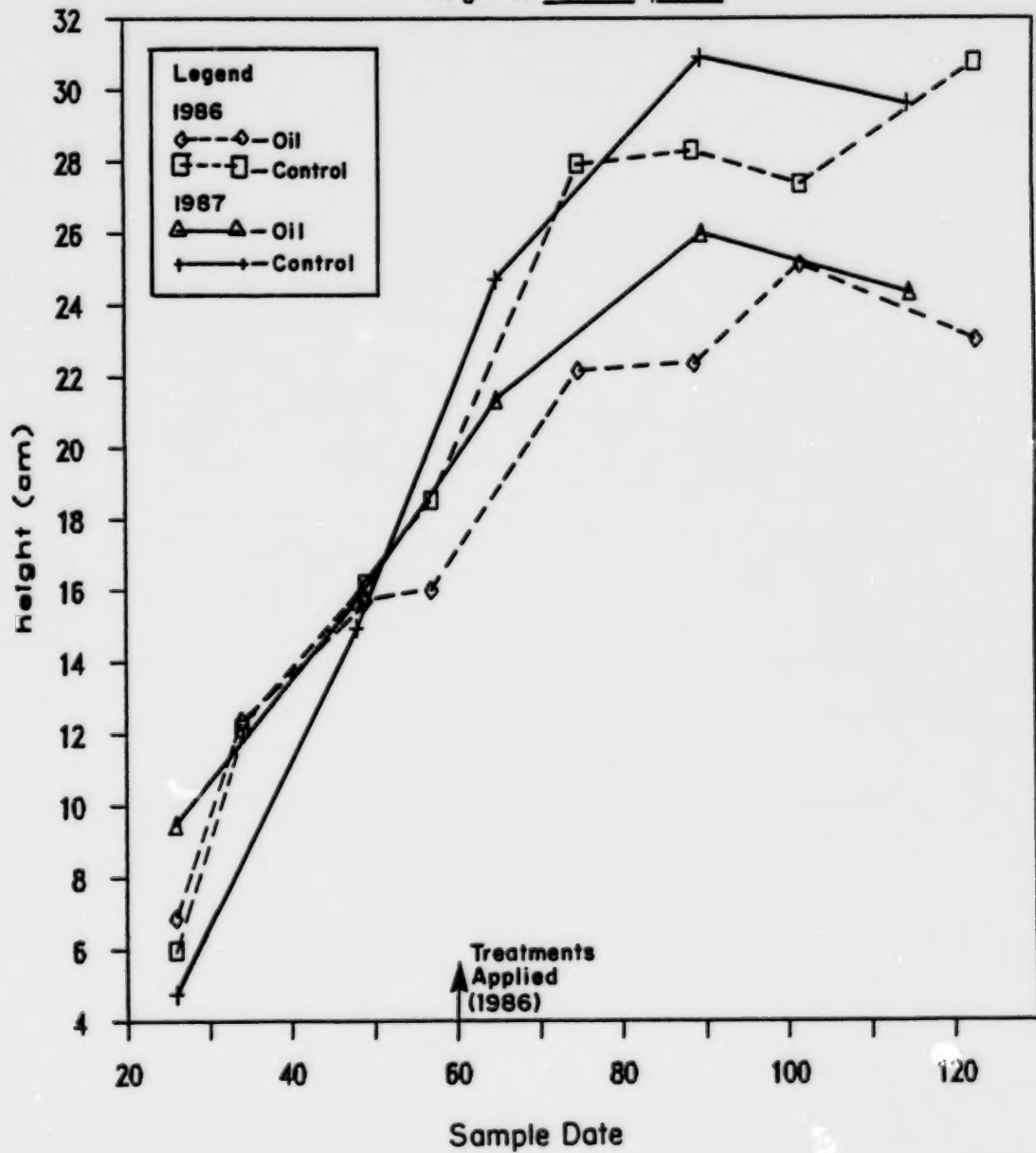
Height of *Spartina patens*

Figure 3: Plot of mean *Spartina patens* height for the high marsh zone versus time.

Creek Edge

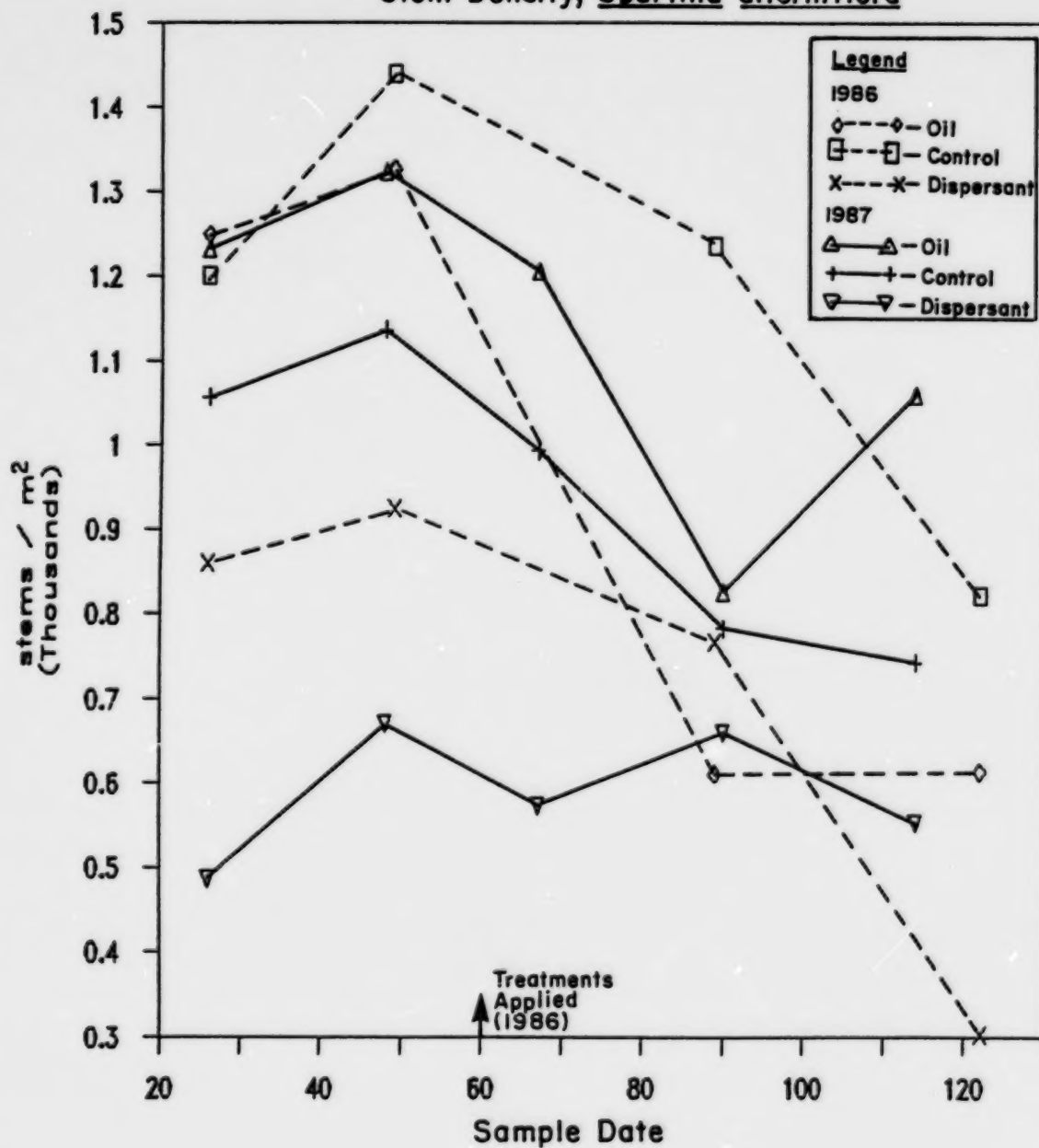
Stem Density, *Spartina alterniflora*

Figure 4: Plot of mean *Spartina alterniflora* stem density for the creek edge zone versus time.

stem density trends for the control and dispersant treated plots. In 1986, stem density was reduced to a mean of 300 stems/m² by the end of the growing season (Day 123) from a maximum of 930 stems/m² (day 49). During 1987 stem density remained relatively stable during the growing season with 550 stems/m² at the end of the growing season (Day 118) and a maximum of 670 stems/m² (Day 48). This data suggests a moderate recovery of stem density during the 1987 growing season. At the current rate of recovery stem density in the dispersant treated plots should return to pretreatment levels within two years of dispersant applications. Stem density in control plots in both 1986 and 1987 decreased gradually during the growing season probably as a result of mortality induced by intraspecific competition. In dispersant treated plots in 1987 stem density remained stable and plants were generally well spaced in the quadrats, suggesting that intraspecific competition was probably reduced in these quadrats resulting in less mortality. On the last two sampling dates in 1987, the stem densities of dispersant treated plots were not significantly different from control stem densities.

In the midmarsh zone (Figure 5) the oil treatment was associated with significant reductions of stem density ($p < 0.001$, ANOVA (89% reduction in stem density by the end of the growing season)). Stem densities of oil treated plots remained significantly lower than controls throughout the 1987 growing season ($p < 0.001$, ANOVA). Stem density early in the 1987 growing season (day 26) was 350 stems/m² which was similar to that noted at the end of the 1986 growing season (230 stems/m²). Over the course of the 1987 growing season Spartina alterniflora stem density increased slowly to 800 stems/m². This appears to indicate that stem density recovered slightly during the 1987 growing season, however, at the end of the sampling period, the mean stem density of the control plots was still 73% higher than that of oiled plots. Complete revegetation of the midmarsh zone will probably take at least five years assuming that the current recovery rate is maintained.

Oil treatments in the high marsh zone (Figure 6) were associated with significant reductions in stem density in 1986. In 1987, oil treated quadrats had significantly lower mean stem densities on all but the first sampling date. At the end of the 1986 growing season mean stem density of oil treated plots was 48% lower than that of control plots, while at the end of the 1987 growing season it was only 32% lower than that of control plots indicating that some recovery had occurred. Complete revegetation of the high marsh might be expected to occur within three to four years of treatment application assuming the current rates of recovery are maintained.

Mid Marsh

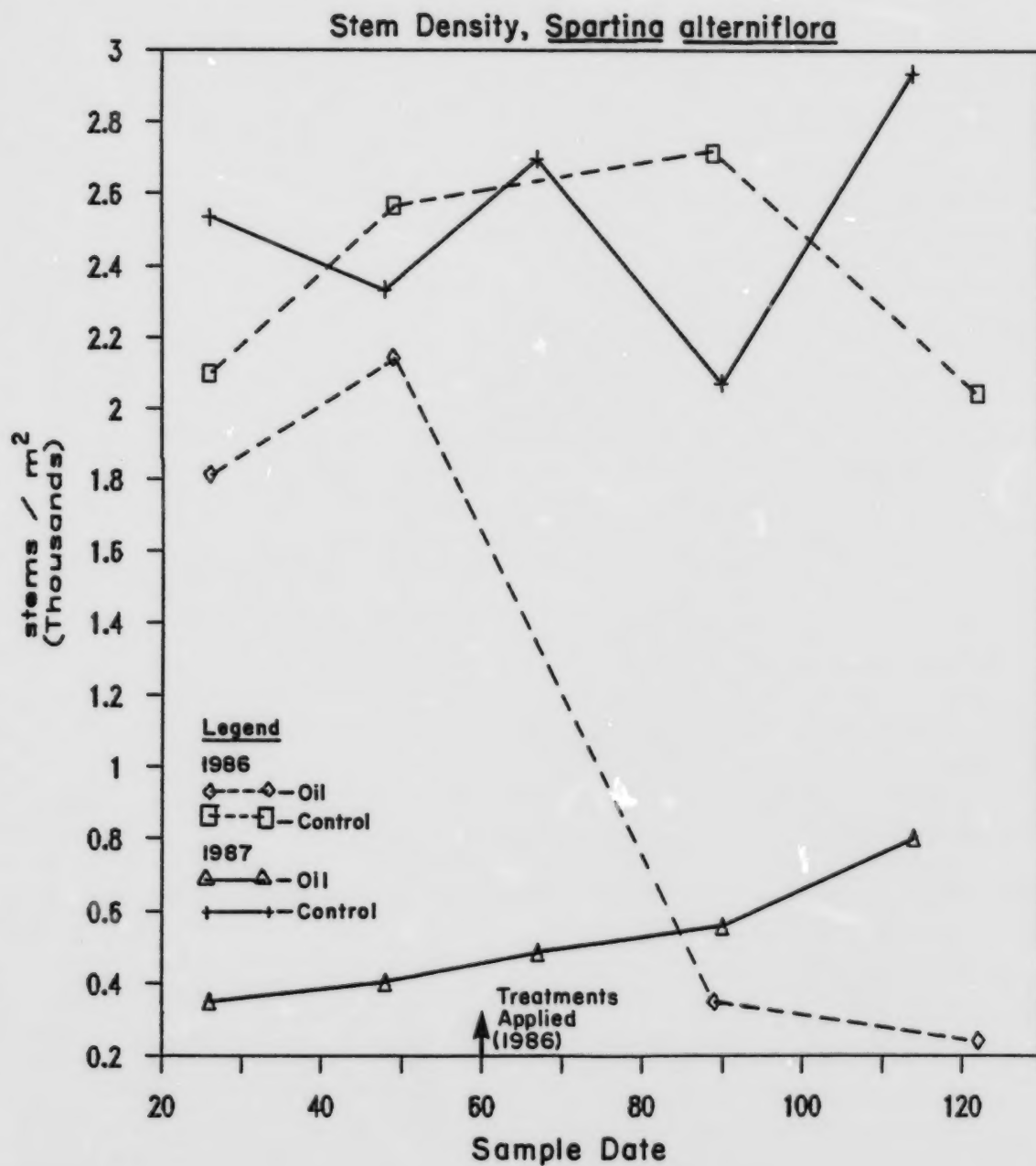


Figure 5 : Plot of mean Spartina alterniflora stem density for the midmarsh zone versus time.

High Marsh

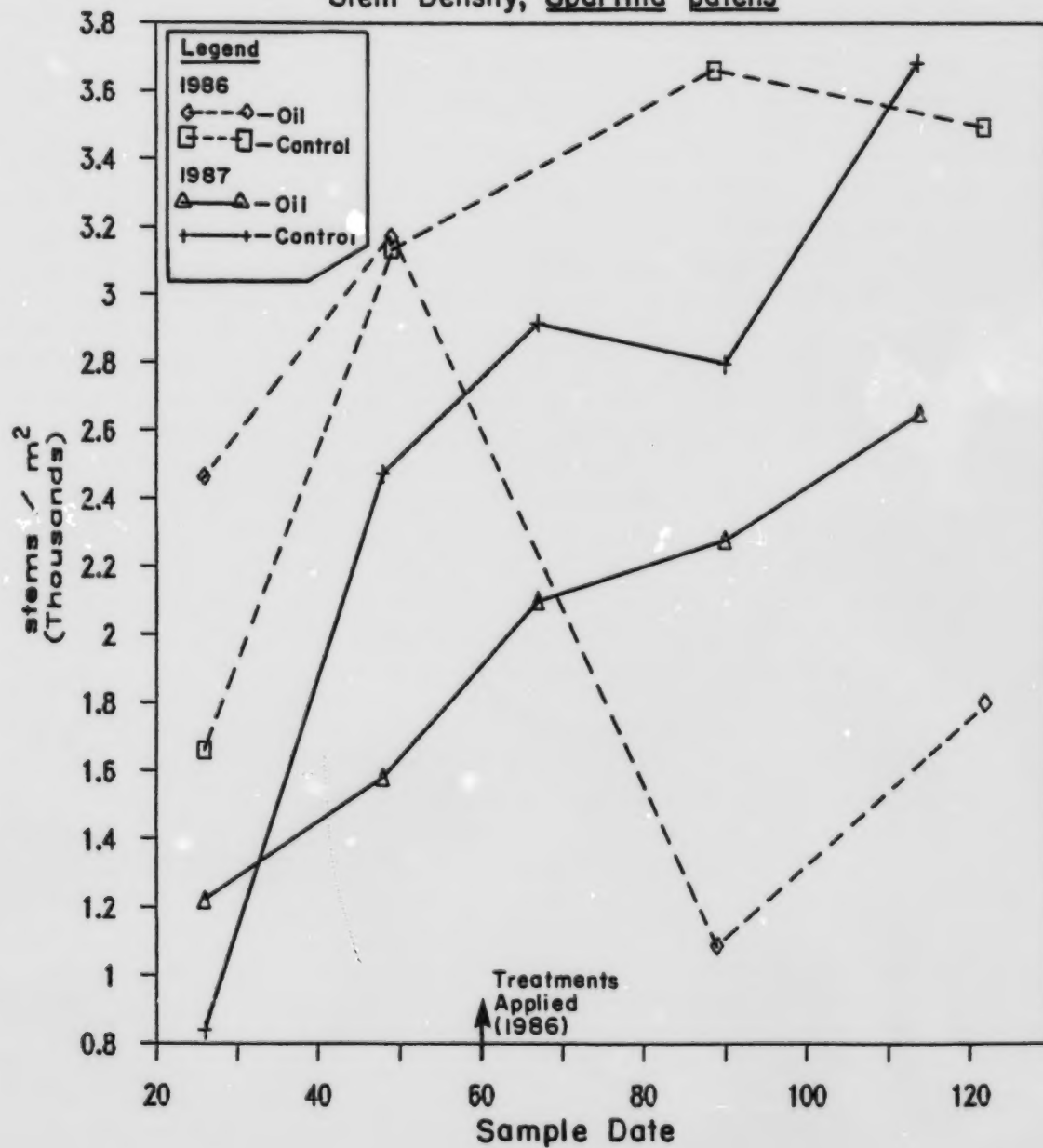
Stem Density, Spartina patens

Figure 6 : Plot of mean Spartina patens stem density for the high marsh zone versus time.

The stem density of flowering *Spartina* plants varied greatly from year to year (Figure 7), however, within years the trends for the various treatments were consistent. In 1986, oil or dispersant treatments caused large declines in flowering shoot density although none of the reductions were significant. For the oil treatments, the largest reduction in density was noted in the creek edge zone (99% reduction) and the smallest in the high marsh zone (64% reduction). Flowering shoot stem density in the midmarsh zone was reduced by 86%. Dispersant treated plots in the creek edge zone exhibited a 95% reduction in density. Similarly, Baker (1971) noted that oiling of *Spartina x townsendii* in the early summer resulted in reduced flowering. This was attributed to oil induced mortality of flower buds or primordia. In 1987, the trend for flowering stem density in 1986 was reversed. Flowering shoot densities for oil and dispersant treated plots in 1987 were equal to or in most instances, higher than control densities from 1986 or 1987. In the creek edge zone, dispersant treated plots had the highest density of flowering shoots, followed by oiled plots then control plots at a ratio of 14:6:1. Flowering shoot densities were significantly higher in the dispersant treated plots ($p=0.004$, ANOVA) but not in the oiled plots. The density of flowering shoots in the midmarsh zone was 45 times higher in oiled plots than in control plots, and in the high marsh zone it was 1.5 times higher in oiled plots than in control plots. These differences however, were not significant in either vegetation zone.

In all vegetation zones, oil treatments induced considerable, although not statistically significant, increases in flowering stem density in 1987. Lack of significance was attributable to the low number of replicates and high variance within treatments. Increases in flowering shoot density appeared to be related to reductions in stem densities noted for the oil and dispersant in 1986 which may have decreased the degree of intraspecific competition allowing more resources to be channeled into reproductive organs. Similar increases in flowering shoot density have been noted in *Spartina anglica* stands in Britain following cutting or trampling damage (Hubbard, 1970).

Biomass

Total above-ground living biomass data from the creek edge zone (Figure 8), indicated that the oil treatment had no significant effect on total above-ground living biomass in either 1986 or 1987. Plots treated with dispersant had significantly less biomass in 1986 ($p=0.017$, ANOVA) but recovered to control levels by the end of the 1987 growing season. In the midmarsh zone in 1986 (Figure 8), total above-ground living biomass in oiled plots was reduced to 15% of control plot biomass (significant $p=0.003$, ANOVA). In 1987 oiled

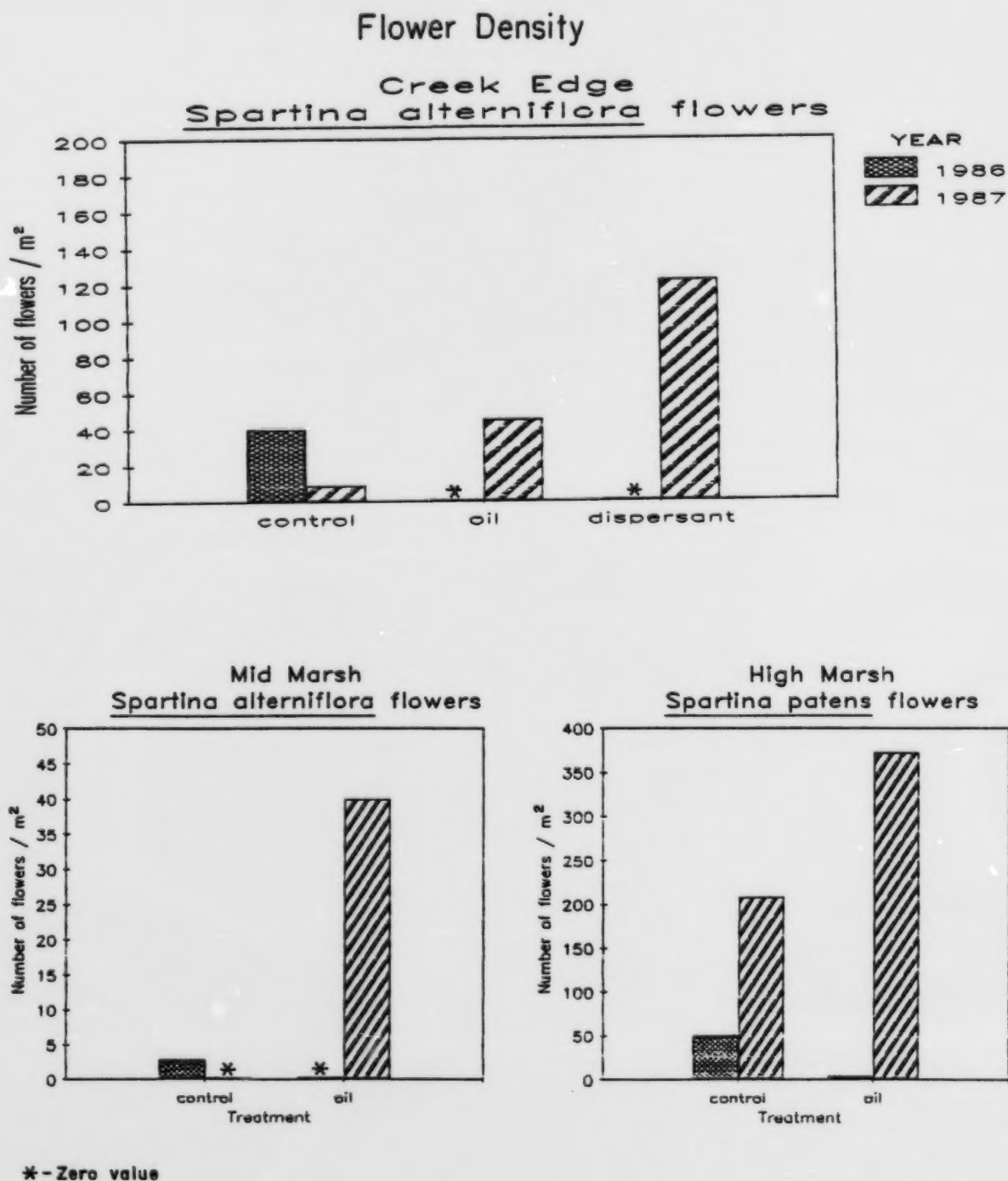
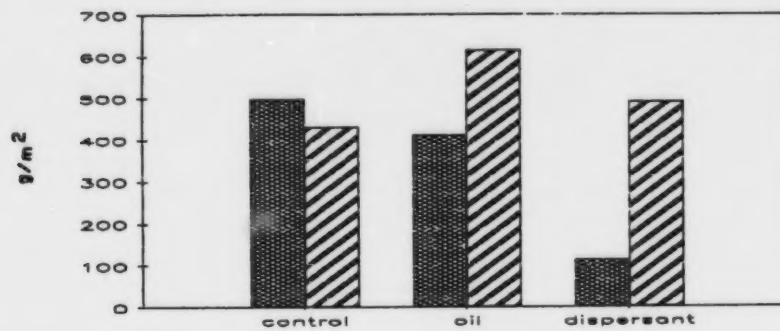
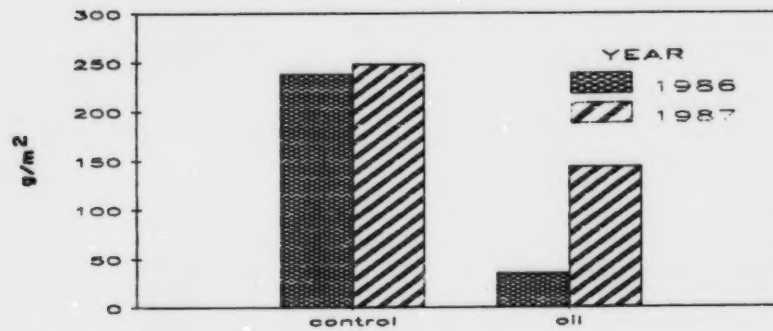


Figure 7 : Histograms of mean flowering shoot density in the creek edge, midmarsh and high marsh zones.

CREEK EDGE BIOMASS



MID MARSH BIOMASS



HIGH MARSH BIOMASS



Figure 8: Histograms of total above-ground biomass in the creek edge, midmarsh and high marsh zones.

plots had recovered to 58% of control biomass values and were not significantly different from the control plots. Total above-ground living biomass for oiled plots in the high marsh zone (Figure 8) was reduced to 69% of control values in 1986. This reduction was not significant. Total above-ground living biomass in the oiled plots increased in 1987, however, control values also increased so that the relative amount of biomass in the oiled plots remained stable at 69% of control plot values. The variance of both control and oil treated high marsh plots declined substantially in 1987 resulting in a significant difference between the treatments ($p=0.011$, ANOVA).

These data suggest that the oil treatments had little impact on biomass production in the creek edge zone. In the more stressful midmarsh zone the oil treatment had severe impacts in 1986 but appeared to recover in 1987. Data from the high marsh zone suggests a moderate impact in 1986 but with relatively little recovery in 1987. The creek edge dispersant treatment was responsible for a major reduction in total above-ground living biomass in 1986, however, it recovered rapidly to control levels by the end of the 1987 growing season.

Species Cover

Spartina alterniflora cover in the creek edge zone was significantly reduced by the oil treatment in 1986 (Figure 9; In 1987, S. alterniflora cover in the oiled plots was not significantly different from the control values, however, this apparent recovery was attributable more to a reduction in control cover in 1987 than to an increase in the cover of oiled plots in 1987. A similar trend was noted for S. alterniflora cover in dispersant treated plots. Cover reductions were significant throughout the 1986 growing season. Cover values noted during the 1987 growing season were similar to those recorded in 1986, however, on days 70 and 90 these values were not significantly different from the 1987 control values as a result of the reduction of control cover values in 1987. Drought conditions during the 1987 growing season may have contributed to this decline. If drought was a factor affecting the growth of controls, it would also be expected to affect growth in the treated plots. The apparent lack of recovery in these plots may be the result of an overall growth reduction caused by the drought.

In the midmarsh zone in 1986 the oil treatment was associated with significant reductions in the cover of Spartina alterniflora (Figure 10) on days 75 ($p<0.001$, ANOVA) and 102 ($p<0.001$, ANOVA). Mortality tended to occur in patches with areas of complete mortality bordering areas where mortality was very light. During the 1987 growing season no apparent expansion of surviving Spartina patches was

Creek Edge Cover

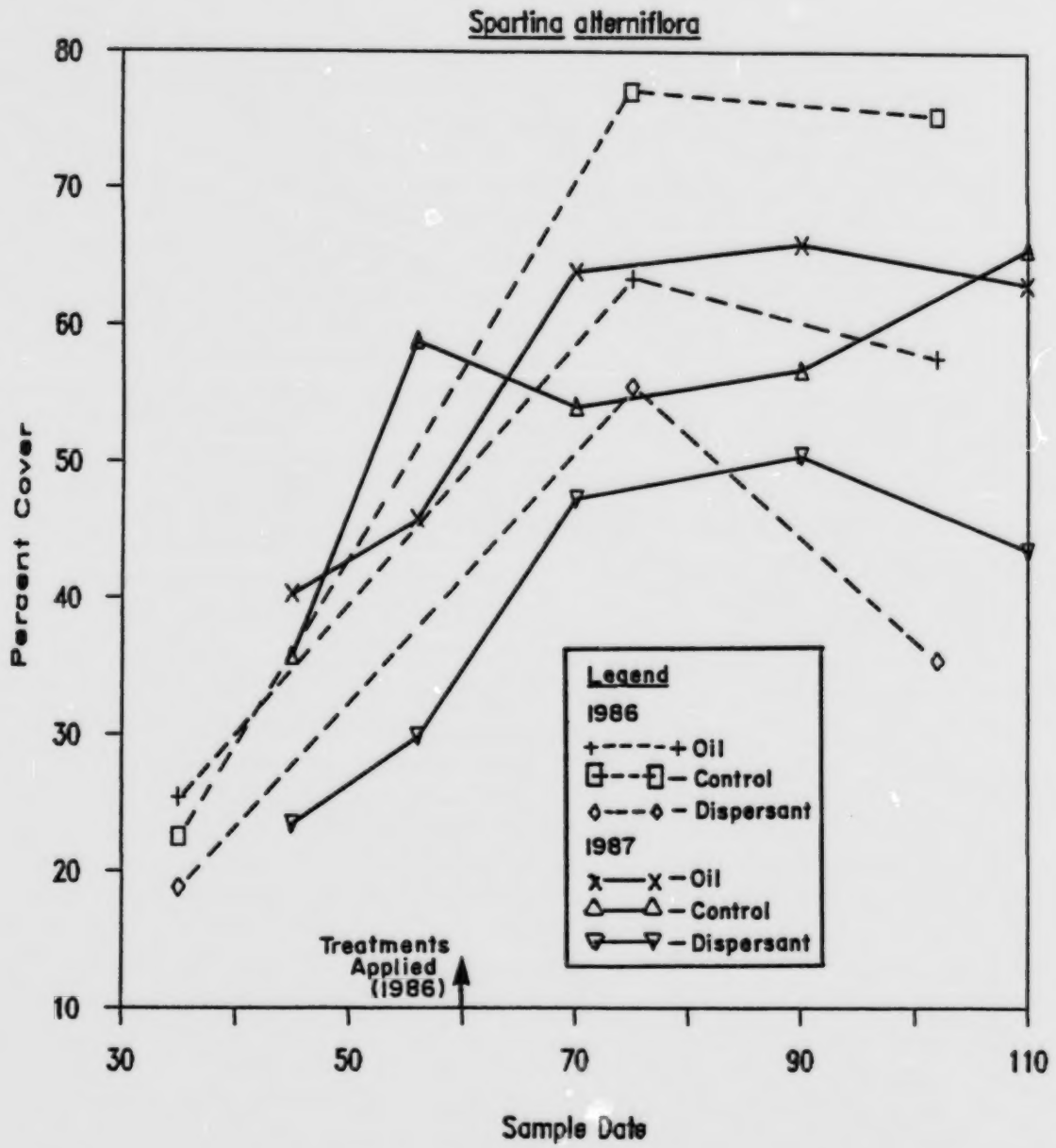


Figure 9 : Plots of mean *Spartina alterniflora* cover in the creek edge zone versus time.

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Mid Marsh Cover

Spartina alterniflora

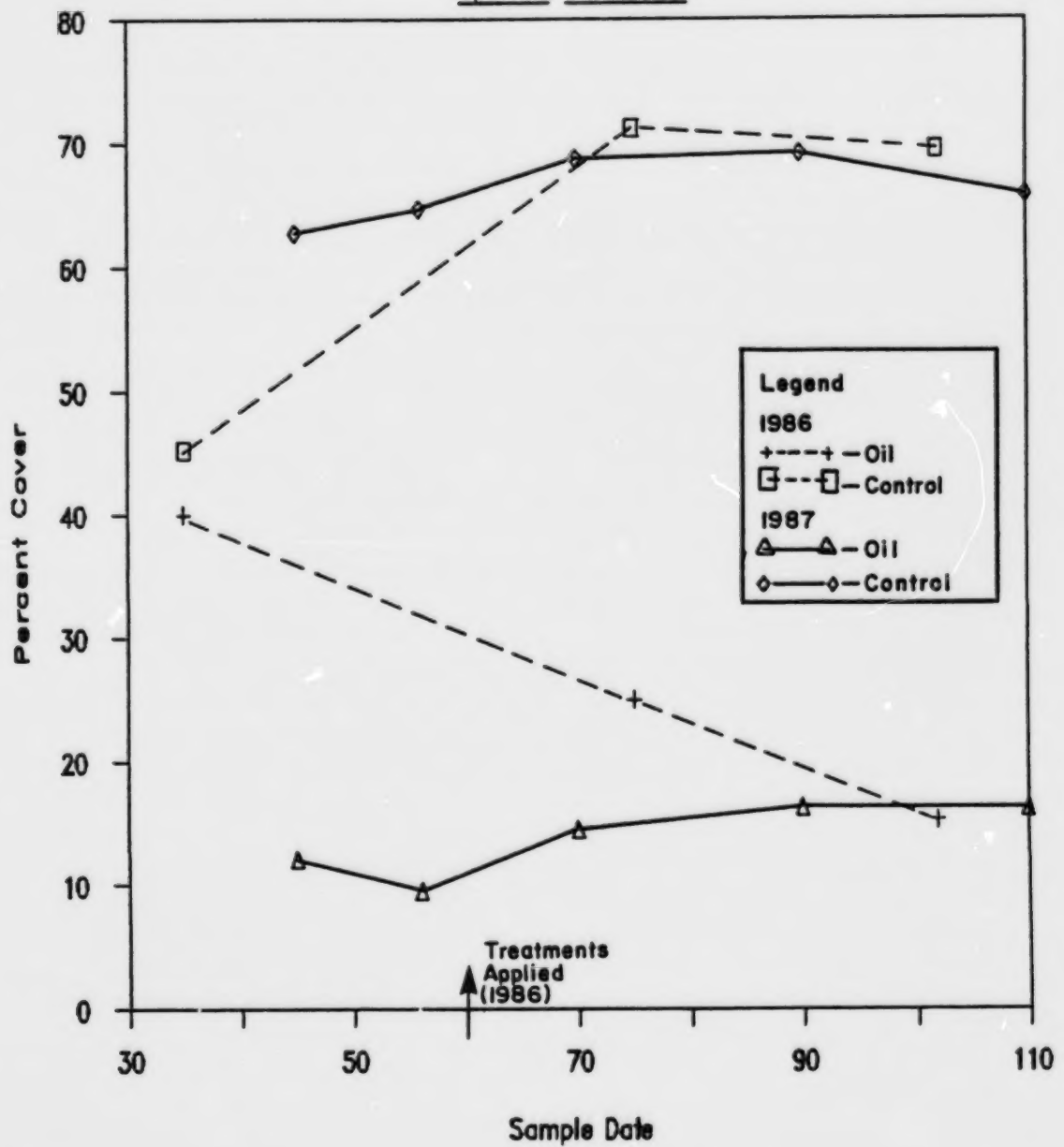


Figure 10: Plot of mean Spartina alterniflora cover in the midmarsh zone versus time.

noted, nor were new patches established, consequently, the cover noted at the end of the 1987 growing season was similar to that noted at the end of the 1986 growing season. A small increase in stem density was noted during the 1987 growing season (Figure 5). This increase was probably restricted to the interior and periphery of existing patches accounting for the lack of patch expansion noted in the cover data. During the 1987 growing season Spartina alterniflora cover in the oiled plots was significantly lower than in control plots on all sampling dates ($p < 0.001$, ANOVA). The large reduction of S. alterniflora cover in the midmarsh zone relative to the creek edge zone was probably attributable to the higher physiological stress levels encountered in the midmarsh zone. S. alterniflora in this zone was unable to tolerate the additional stress associated with the oil treatment.

In the high marsh zone Spartina patens cover in the control and oil treated plots displayed little change between 1986 and 1987 (Figure 11). In 1986, the oil treated plots had significantly higher cover than control plots on day 35 (pretreatment, $p = 0.048$, ANOVA), however, within fifteen days of oil application, cover in the oiled plots had declined to 90% of control values. S. patens cover was significantly lower than control values ($p = 0.005$, ANOVA) on day 102. A similar trend was observed in 1987. S. patens cover in the oiled plots was significantly higher than in control plots ($p = 0.011$, ANOVA) at the beginning of the growing season. It declined briefly on day 56 but recovered to 1986 oiled plot values by day 90. S. patens cover in oiled plots was significantly lower than in control plots on days 70 ($p = 0.001$, ANOVA) and 110 ($p = 0.031$, ANOVA).

This evidence suggests that there was no recovery of S. patens in the high marsh oiled plots. Reinvasion of bare patches by S. patens tillers is slow (Bertness and Ellison, 1987) and this species generally has very poor seed set as a result of seed predation by insects (Bertness et al., 1987). S. patens stands also maintain high detritus cover (up to twice the cover of living plants) which can interfere with the recolonization of patches of dead S. patens by shading of seedlings. Removal of this detritus has been demonstrated to increase stem density by a factor of 4 (Lane et al., 1987). The detritus layer in the oiled plots remained intact throughout 1986 and 1987.

Salicornia europaea and Suaeda maritima were the most common species in the creek edge study plots other than the two Spartina species. Generally, they accounted for less than 10% of the total cover of the plots. During the 1986 growing season these annual species were uncommon in the creek edge zone (Figure 12). In 1986, Salicornia was eliminated by the oil treatment but appeared to be

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High Marsh Cover

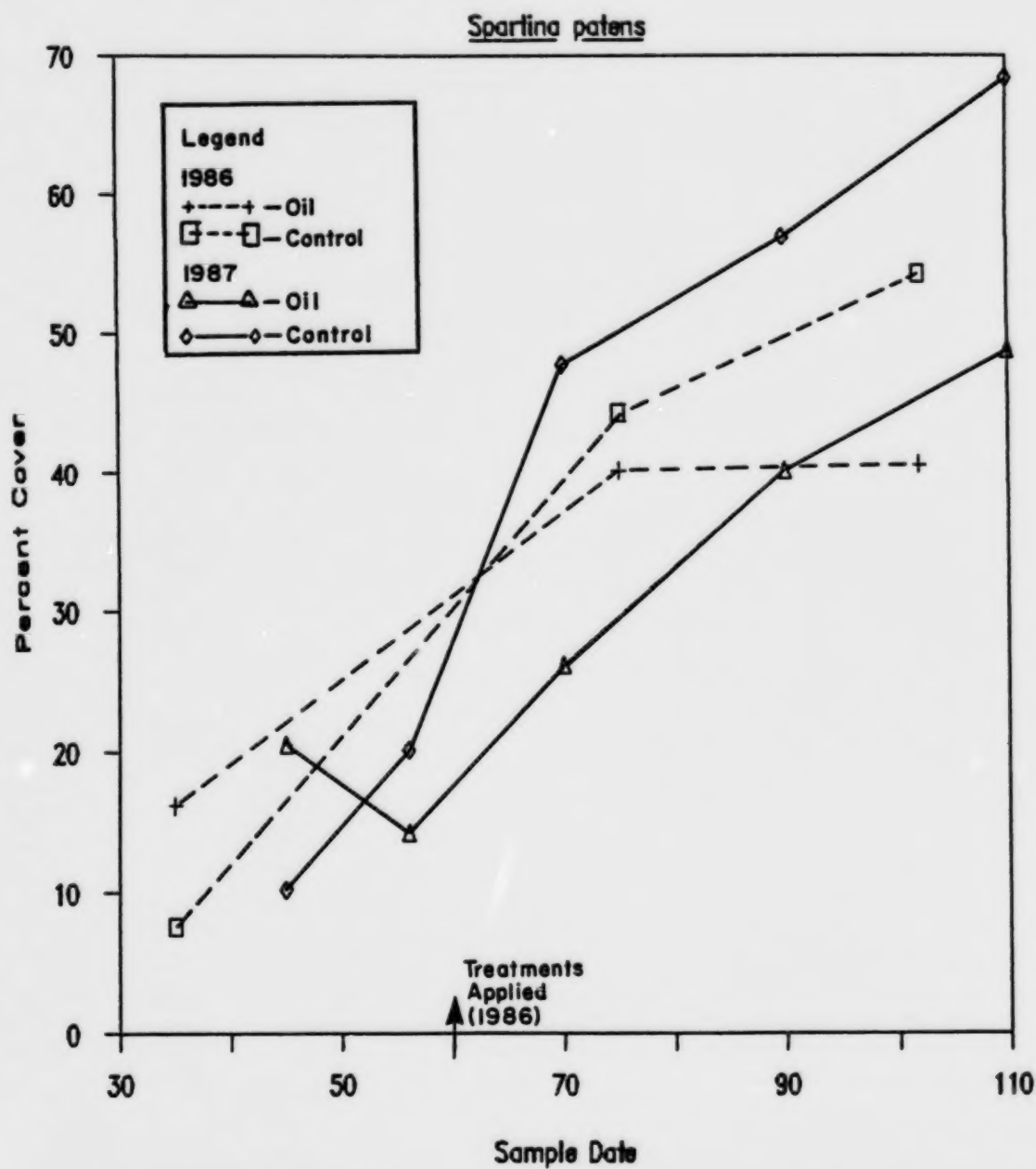


Figure 11: Plot of mean Spartina patens cover in the high marsh zone versus time.

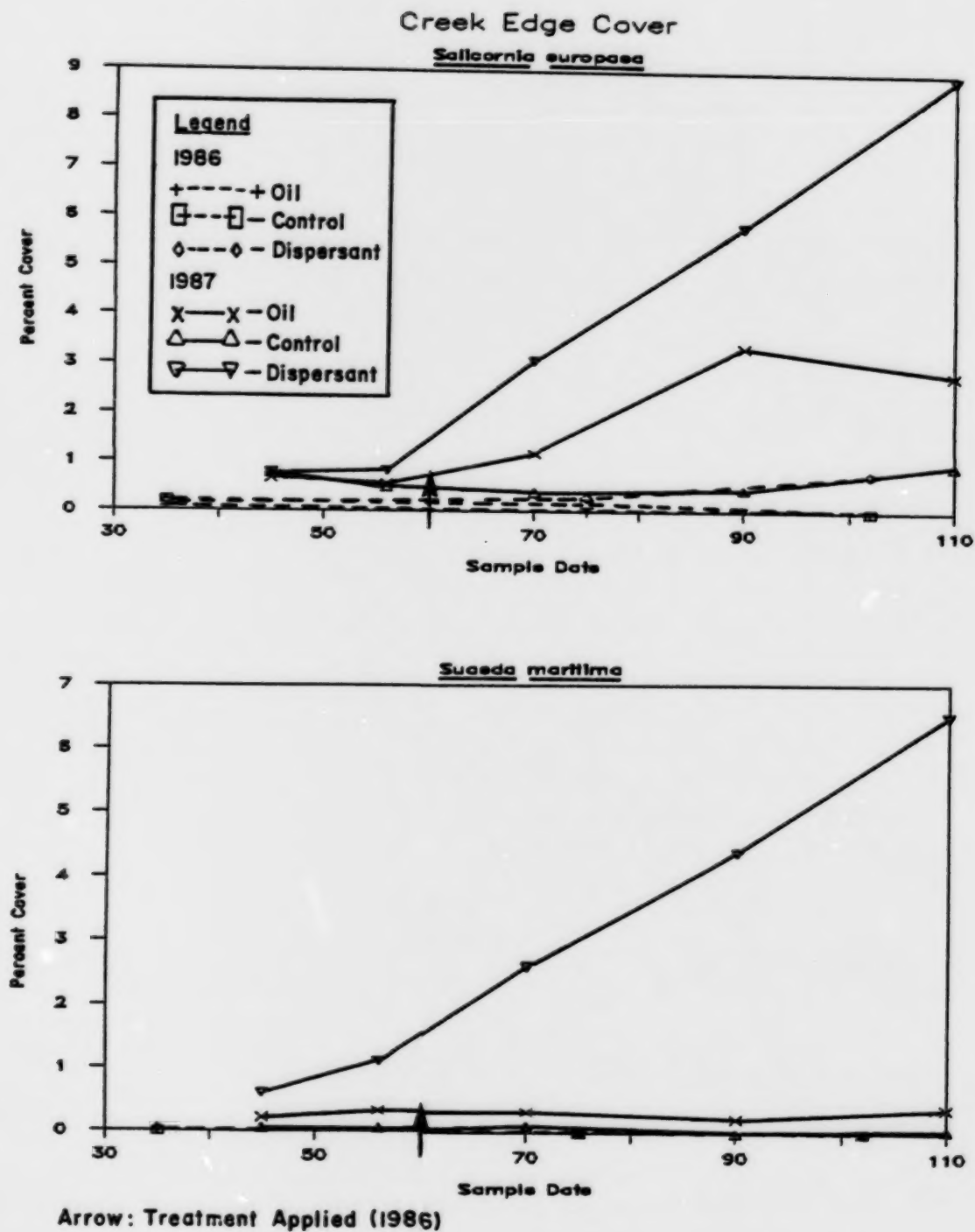


Figure 12 Plots of mean Salicornia europaea and Suaeda maritima cover in the creek edge zone versus time.

unaffected by the dispersant treatment. Cover values remained low and variable through the 1986 growing season, consequently none of these changes were statistically significant. In 1987, Salicornia cover increased in all treatments. Cover in control plots in 1987 was on average twice as high as control cover in 1986. This increase may have been attributable to sampling disturbance at the edges of the plots. It may also have been related to the drought induced reductions in Spartina cover mentioned above. Salicornia is an early successional species which is very tolerant of high salinity (Brereton, 1971). Drought conditions may have increased salinity to a point where it was stressful to Spartina but within the tolerance range of Salicornia. Salicornia cover in the oil and dispersant treated plots displayed similar trends during the 1987 growing season. Cover remained stable between days 45 and 56 after which it began to increase rapidly. In the oiled plots, cover increased until day 90 after which it stabilized. End of season cover was 3.0 times higher than control values. Cover in the oiled plots was significantly higher than controls on days 70 ($p=0.044$, ANOVA) and 90 ($p=0.023$, ANOVA). In the dispersant treated plots, Salicornia cover increased until the end of the sampling period. End of season cover in the dispersant treated plots was 9.5 times higher than control plots and 3.2 times higher than oil treated plots. Cover in dispersant treated plots was significantly higher than in control plots on days 70 ($p<0.001$, ANOVA), 90 ($p<0.001$, ANOVA) and 110 ($p<0.001$, ANOVA).

The abundance of Salicornia was inversely related to the cover of Spartina alterniflora. A strong correlation ($r=-0.815$) was noted between the square root of Spartina alterniflora cover and the square root of Salicornia cover. Salicornia normally grows on open mudflats or in areas where stranded debris has eliminated the dominant vegetation (Bertness and Ellison, 1987). Mortality of Spartina shoots associated with the oil and dispersant treatments may have opened up the canopy enough to allow the establishment and maximum growth of this species. There was a curvilinear relationship between the cover of Salicornia and S. alterniflora cover. Salicornia cover was affected relatively little by reduction of S. alterniflora cover to as low as 50% but increased rapidly when Spartina cover dropped below 50%.

Salicornia cover in the midmarsh zone did not respond to destruction of the Spartina alterniflora sward as vigorously as noted in the creek edge zone (Figure 13). Spartina cover in the midmarsh zone was reduced to 22% of control values by the oil treatment while the dispersant treatment in the creek edge zone reduced Spartina cover to 47% of control values, yet Salicornia cover was similar in both treatments. The strong negative correlation of Spartina cover and

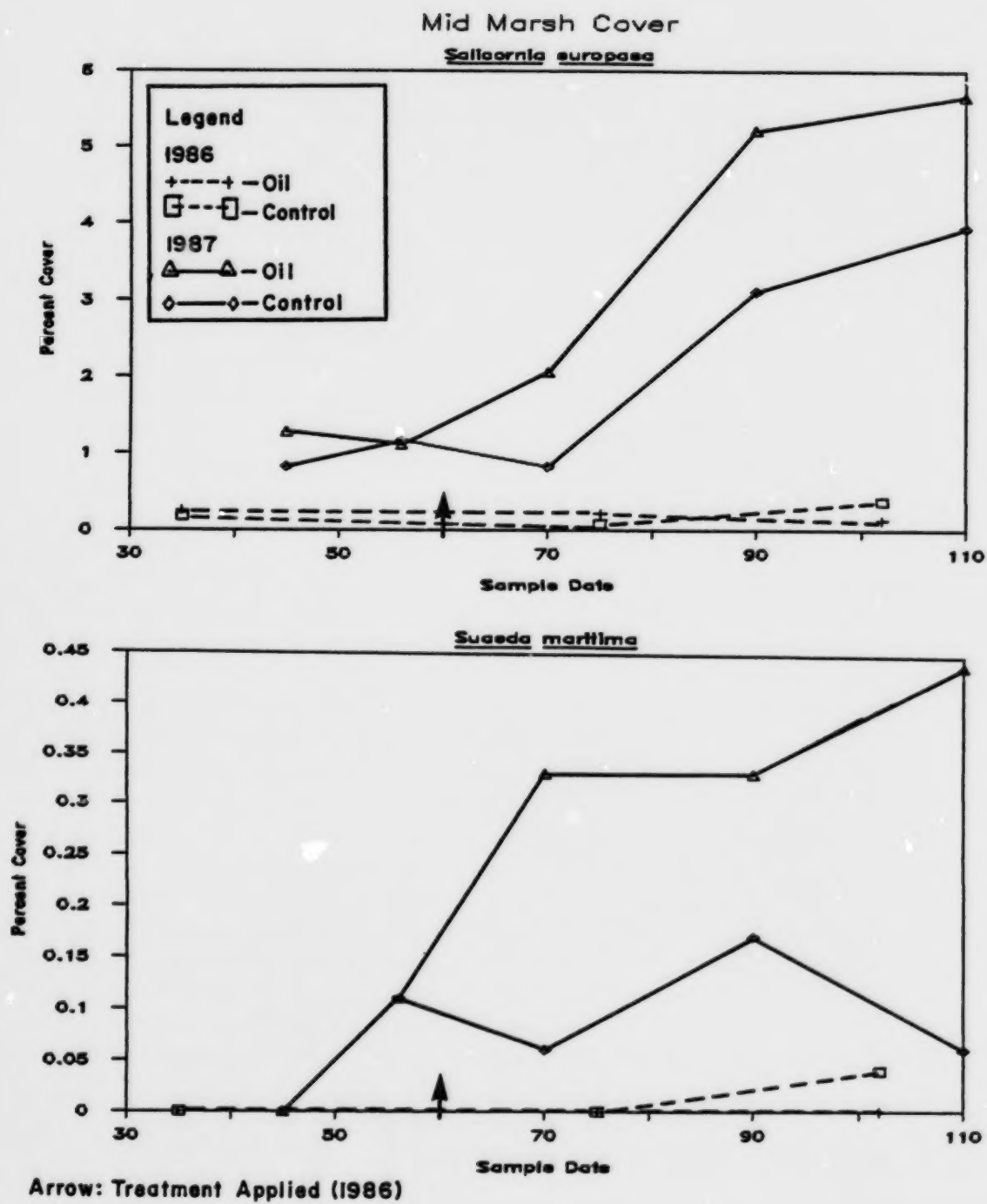


Figure 13: Plots of mean Salicornia europaea and Suaeda maritima cover in the mid marsh zone versus time.

Salicornia cover noted in the creek edge zone was not noted in the midmarsh zone ($r=-0.656$). High physiological stress associated with the midmarsh zone accompanied by residual oil toxicity, may have contributed to the relatively poor growth of Salicornia in this zone. This is confirmed by Brereton (1971) who found that Salicornia grew poorly in soils with low redox potential. A relatively large increase in Salicornia cover was noted in the control plots. The seasonal trend for Salicornia cover in the control plots was similar to that of the oiled plots but averaged 65% as high. This prevented the increase in cover in the oiled plots in 1987 from being statistically significant. Increased Salicornia cover in the control plots may have been attributable to sampling disturbance which permitted the establishment of Salicornia along the edges of the plot and/or drought conditions which reduced the cover of the Spartina sward.

Salicornia cover in the high marsh zone demonstrated little yearly variation in the control plots (Figure 14). In the oiled plots the seasonal trend for Salicornia cover in 1986, was very similar to that of the control plots suggesting little oil induced mortality. In 1987, an increase in Salicornia cover was noted in the oiled plots. Salicornia cover was significantly higher in the oiled plots than in the control plots on all sampling dates ($p = 0.01$, ANOVA) except day 56. This is somewhat misleading since Salicornia cover was consistently higher in the oiled plots than in control plots both before and after treatment applications. In 1986, Salicornia cover in oiled plots was significantly higher than in control plots on days 35 ($p=0.014$, ANOVA) and 102 ($p=0.001$, ANOVA). There was a very strong negative relationship between Spartina patens cover and Salicornia cover ($r=-0.942$) suggesting that increases in Salicornia cover were related to reductions in S. patens competition.

Suaeda cover responded to the oil and dispersant treatments similarly to Salicornia (Figure 12). In 1986, Suaeda was present in only one dispersant plot on day 35. It disappeared from the creek edge zone following the dispersant treatment application. In 1987 Suaeda occurred sporadically in the control plots, remaining at low levels throughout the growing season. In the oiled plots Suaeda was more common, however, its cover remained stable throughout the growing season. Suaeda cover in the oiled plots was significantly higher than control plots on day 56 ($p=0.030$, ANOVA). Few Suaeda shoots grew larger than 5 cm under the well developed Spartina canopy in the oiled plots. Suaeda cover was highest in the dispersant treated plots. Cover increased throughout the growing season, reaching a peak of 6.50%. Suaeda cover in dispersant treated plots was significantly higher than that of control plots on all sampling dates in 1987 ($p < 0.001$, ANOVA). There was a strong negative correlation ($r=-0.825$)

High Marsh Cover

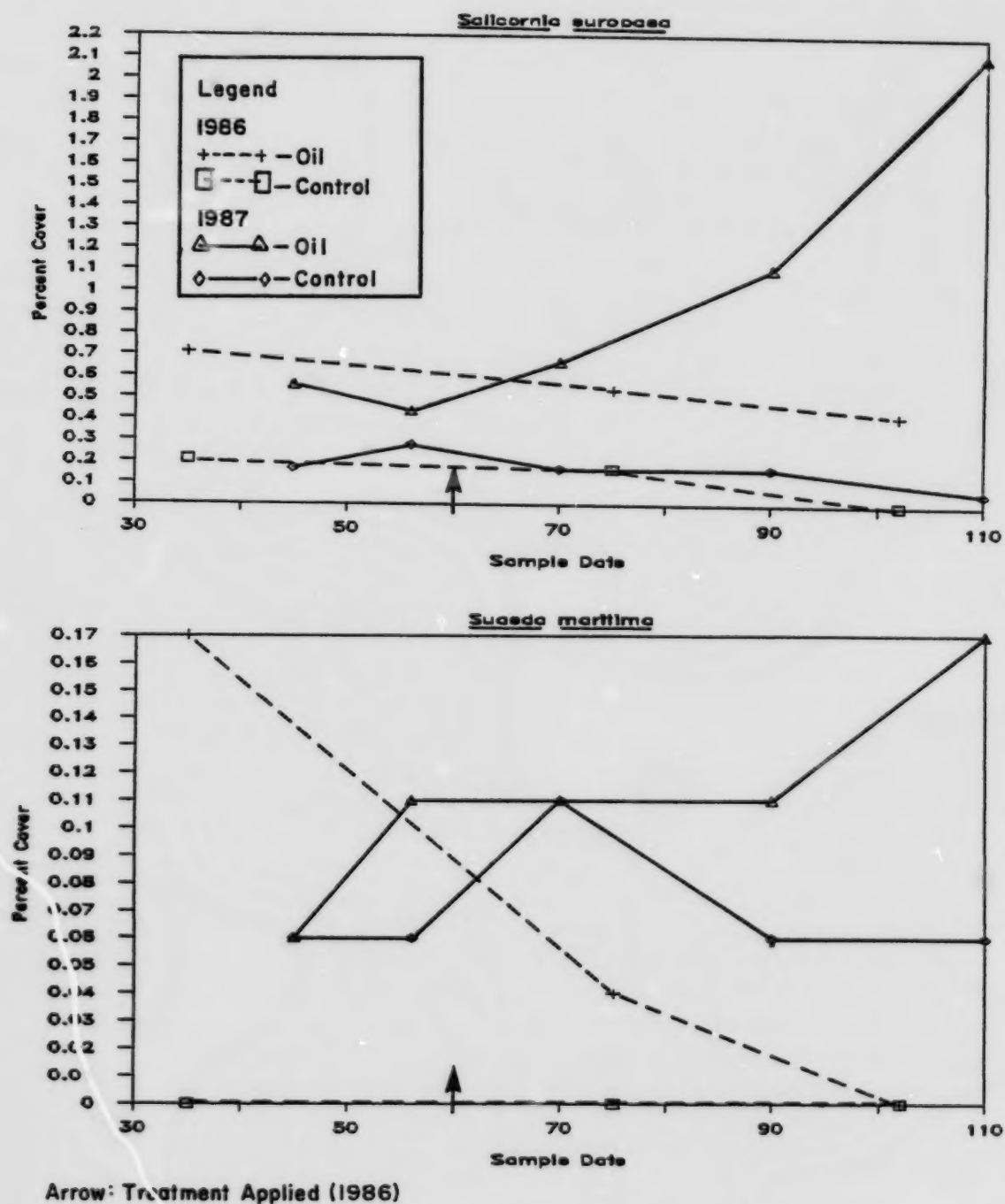


Figure 14: Plots of mean Salicornia europaea and Suaeda maritima cover in the high marsh zone versus time.

between the square root of Suaeda cover and the square root of Spartina alterniflora cover suggesting that this species was responding to the removal of the dense Spartina canopy. As was noted for Salicornia, Spartina cover reductions of at least 50% were required to evoke a large increase in Suaeda cover.

In the mid marsh zone Suaeda was noted in only one control plot during the 1986 growing season (Figure 13). In 1987, Suaeda was absent in control and oiled plots on day 43 but appeared in both treatments by day 56. Suaeda cover in the oiled plots increased throughout the growing season while cover in the control plots stabilized after day 56. Suaeda cover in the oiled plots was significantly higher than in the control plots on days 70 ($p=0.044$, ANOVA) and 110 ($p=0.011$, ANOVA). Suaeda cover in the midmarsh oiled plots was equivalent to that found in oiled plots in the creek edge zone. High Suaeda cover would be expected in the midmarsh zone since Spartina mortality was much higher there. The coefficient of correlation between the square root of Spartina cover and the square root of Suaeda cover in this zone was only -0.717 as opposed to -0.825 in the creek edge zone. The combination of a normally hostile environment for plants combined with residual oil toxicity (as outlined for Salicornia) may have restricted the establishment and growth of Suaeda in the midmarsh oiled plots.

In the high marsh zone, Suaeda was present only in the oiled plots in 1986 (Figure 14). Suaeda cover in the oiled plots declined after oil application and had disappeared from the plots by the last sampling date. This data suggests that Suaeda was sensitive to the oil treatment. Baker (1971) noted that oil treatments applied during the growing season caused severe reductions in Suaeda maritima cover. In 1987, Suaeda cover increased in both the control and oiled plots with the highest cover values noted in the oiled plots. These differences were not significant. There was a moderately strong negative relationship between Suaeda cover in the high marsh zone and Spartina patens cover ($r=-0.769$).

Discriminant analyses were conducted on the cover data collected in each vegetation zone. The analysis for the Creek edge zone included control, oil and dispersant treatments, therefore, the results were presented in two dimensions. Figure 15 presents a scatter plot for all samples with detritus excluded. The first axis separated dispersant treated plots (represented by 3's) from oiled plots (2's) and control plots (1's). The second function separated oiled plots from control and dispersant plots. Separation was highly significant along both axes (Wilks' lambda, $p<0.00005$). The first axis accounted for 72% of the variance explained, while the second accounted for 28%. Table 1 presents the coefficients of the

Creek Edge
Discriminant Function Scatter Plot

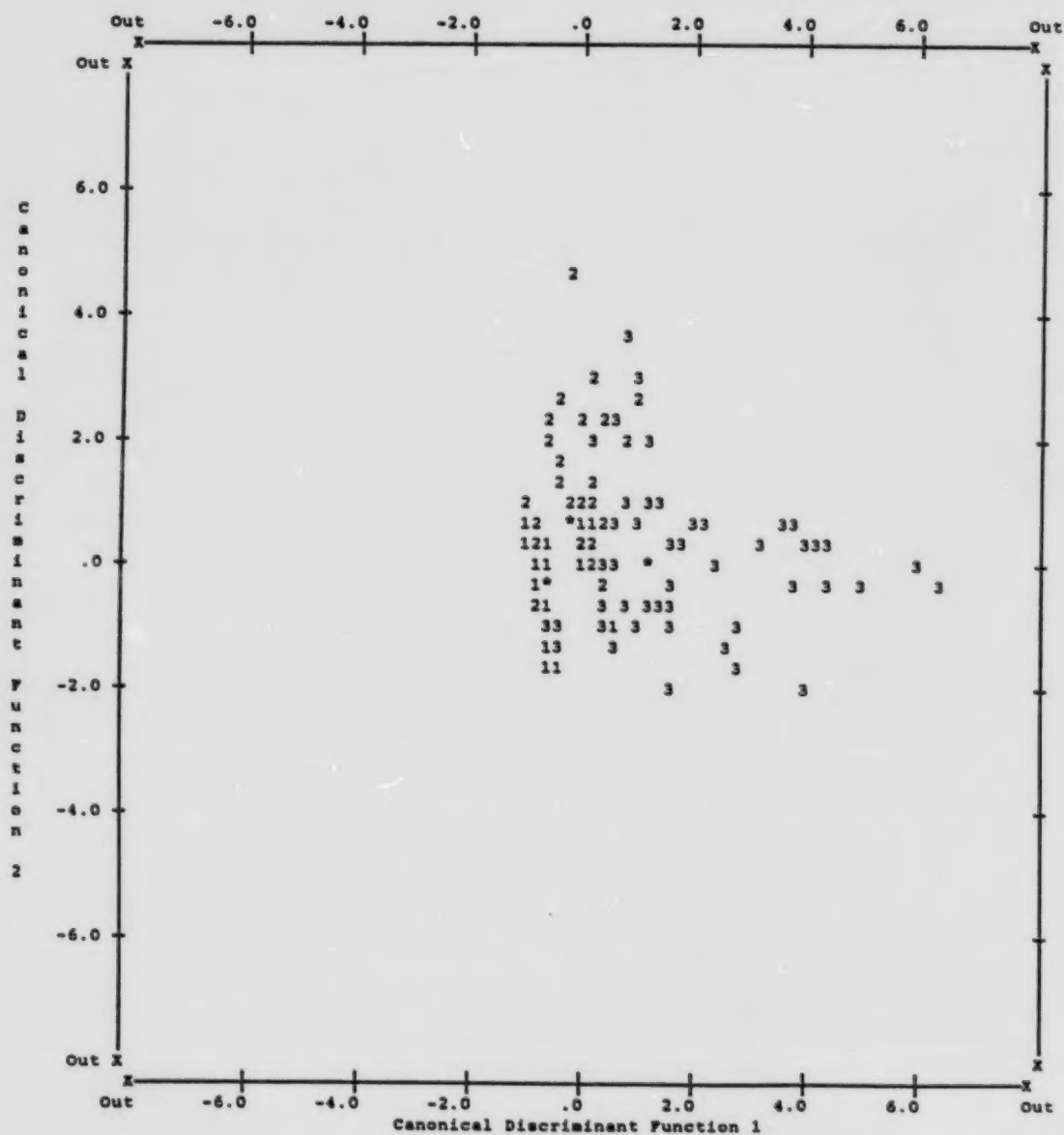


Table 1. Standardized canonical discriminant function coefficients (SCDFC) and pooled-within-groups correlations between species and canonical discriminant functions (CORR). Species cover values were used in the analyses for the three vegetation zones.

Species	CREEK EDGE			
	SCDFC		CORR	
	Function 1	Function 2	Function 1	Function 2
<u>Spartina alterniflora</u>	-0.108	0.659	-0.197	0.659*
<u>Spartina patens</u>	0.153	0.684	0.052	0.690*
<u>Salicornia europaea</u>	-0.190	0.259	0.605*	0.247
<u>Atriplex patula</u>	-0.006	0.086	0.254	0.189
<u>Suaeda maritima</u>	0.918	-0.019	0.885*	0.084
<u>Plantago juncooides</u>	0.437	-0.114	0.637*	-0.146
<u>Glaux maritima</u>	-0.020	0.028	0.193	-0.044

Species	MIDMARSH	
	SCDFC	CORR
	Function 1	Function 2
<u>Spartina alterniflora</u>	0.999	0.867
<u>Spartina patens</u>	0.432	0.115
<u>Salicornia europaea</u>	0.129	-0.141
<u>Atriplex patula</u>	-0.162	-0.287
<u>Suaeda maritima</u>	-0.205	-0.191
<u>Triglochin elata</u>	0.106	0.123
<u>Limonium nashii</u>	-0.061	-0.063

Species	HIGH MARSH	
	SCDFC	CORR
	Function 1	Function 2
<u>Spartina alterniflora</u>	-0.280	-0.307
<u>Spartina patens</u>	0.151	0.001
<u>Salicornia europaea</u>	0.903	0.886
<u>Atriplex patula</u>	0.152	0.343
<u>Suaeda maritima</u>	-0.109	0.102
<u>Triglochin elata</u>	-0.053	0.058
<u>Festuca rubra</u>	0.148	0.147
<u>Glaux maritima</u>	0.198	0.242

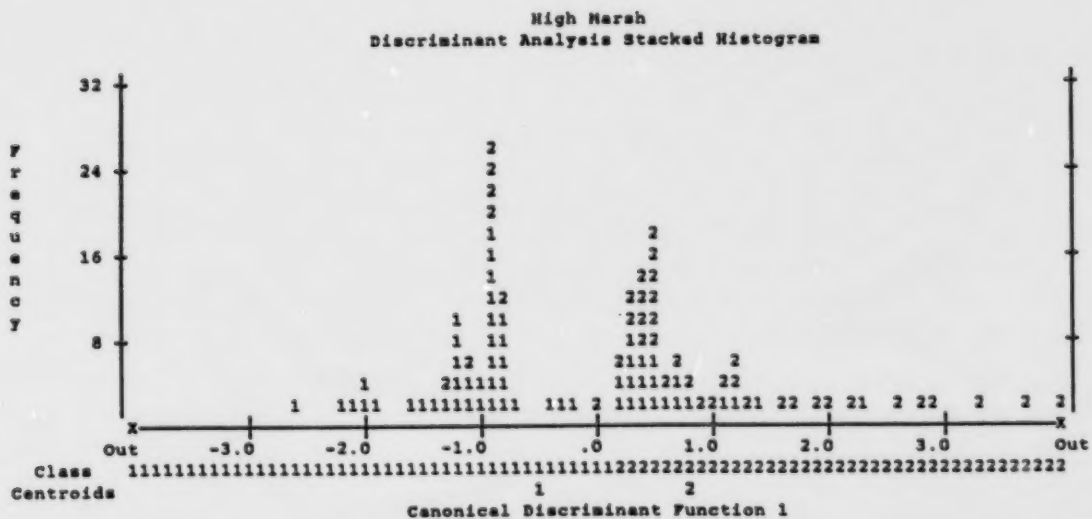
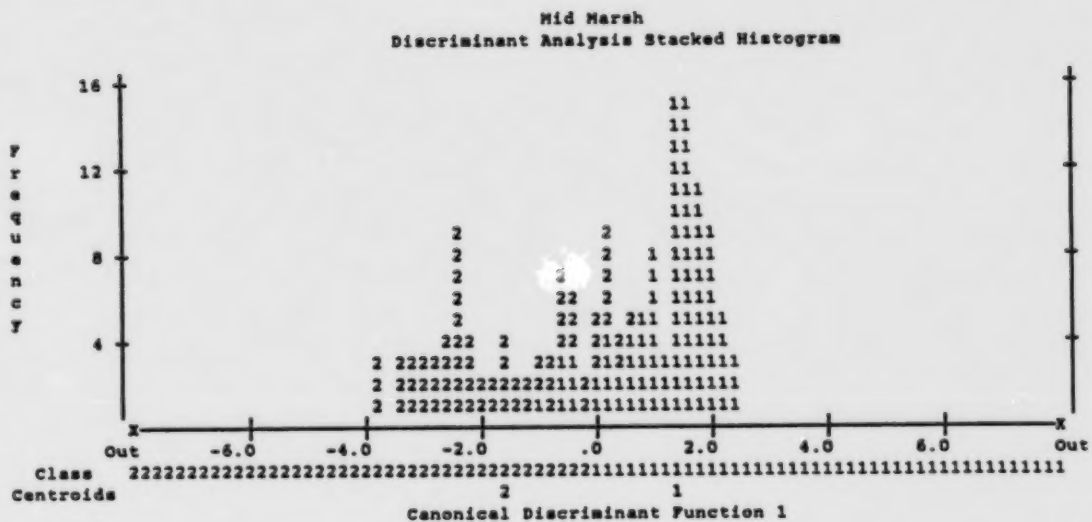
standardized canonical discriminant function and the correlation of each species with each function. The asterisks with each correlation indicate which axis the species is most closely associated. For function 1 which separated dispersant treated plots from other treatments, Suaeda maritima, Plantago juncoides and Salicornia europaea were most important. Separation of the control and oil treated plots was most strongly determined by Spartina alterniflora and S. patens. For each point the probability of belonging to each treatment can be assessed. Each data point can be assessed as to whether it matches its treatment, or is more similar to another treatment. Counting the number that are assessed as misclassified provides an impression of the separation (or overlap) of the ranges resulting from treatment. For the creek edge zone, without standing dead cover incorporated, 97 of the 255 plots were considered misclassified.

The analysis which included standing dead yielded similar results. Both axes were highly significant with detritus associated with the second (control-oil) axis. The inclusion of standing dead cover in the analysis increased both the total variance and the proportion explained by axis 2.

These results indicate that the dispersant treatment was responsible for the largest floristic changes in the creek edge zone. These floristic changes were produced by the proliferation of annual species such as Salicornia and Suaeda after severe damage to the Spartina sward. The small degree of variance accounted for by the oil treatment (28%), indicated how little impact the oil treatment had on the creek edge zone. The results of the analysis suggest that the oil treatment had relatively little effect on species composition since the species most correlated with this function were the dominant Spartina species.

The high marsh and midmarsh zones involved only two treatments (control and oil), consequently, only one function can be generated to separate them. In the analysis for the midmarsh zone, separation was highly significant (Wilks' Lambda, $P < 0.00005$) with S. alterniflora having the only strong correlation (Table 1). Figure 16 clearly indicates the degree of separation obtained. A total of 19 out of 162 sampling units were flagged as misclassified. The results for the analysis incorporating standing dead cover were similar. Standing dead cover was negatively correlated with the function.

The high degree of separation for the midmarsh data indicates the severity of oil toxicity in this zone. High correlation with only S. alterniflora indicated both the high degree of oil induced mortality associated with this species and the relatively poor performance of Salicornia and Suaeda in this zone.



Symbols used in Plots

Symbol	Label
1	Control
2	Oil

Figure 16: Stacked histograms of discriminant analysis scores for plot visits in the midmarsh zones and the high marsh zone. Species cover data were used in the analyses.

The results for the high marsh zone were also highly significant (Wilks' Lambda, $P < 0.00005$), but showed more overlap (Figure 16) as indicated by the higher proportion of misclassifications (48 of 162). Salicornia europaea was highly correlated with the function, while Atriplex patula had a moderate positive correlation and Spartina alterniflora had a moderate negative correlation. Spartina patens showed little correlation with the function (Table 1). When standing dead cover was included in the analysis the number of misclassifications was reduced to 29 out of 162. The resultant function was less strongly correlated with Salicornia europaea (0.65) and the correlation with standing dead was 0.44.

The high degree of misclassification for this zone suggested that the oil treatment had less impact on the floristic composition of this zone than did the oil treatment in the midmarsh zone or the dispersant treatment in the creek edge zone. High correlation of Salicornia with the function indicates that the oil treatment caused enough damage to the S. patens sward to permit a substantial increase in the abundance of Salicornia.

CONCLUSIONS

Plant height data indicated that Spartina height growth in the creek edge zone was relatively unaffected by the oil treatments in both 1986 and 1987 while height growth in the midmarsh and high marsh zones were significantly reduced in 1986. The midmarsh zone was more severely affected by the oil treatments than the high marsh zone. Neither zone appeared to recover during the second growing season. Height growth in the dispersant treated plots in the creek edge zone was significantly reduced during the 1986 growing season but recovered to control levels by the 1987 growing season.

Oil impacts on stem density were still evident in the midmarsh and highmarsh zones in 1987. The largest impacts were associated with the midmarsh zone in both 1986 and 1987. The larger reductions in midmarsh stem density as compared to the creek edge zone were probably attributable to the naturally higher levels of plant stress associated with the midmarsh zone. The additional stress of the oil spill probably taxed the metabolism of the midmarsh plants to the point where most individual stems died. It was difficult to determine the degree of recovery in the creek edge zone since increases in stem density of oiled plots in 1987 were accompanied by large reductions in control stem density. Nevertheless, it appeared that recovery of stem density was most advanced in this zone. The dispersant treatment caused a large reduction of stem density in the creek edge zone in

1986. A moderate increase in stem density was noted for this treatment in 1987.

The density of flowering shoots was substantially reduced (although not significantly) in 1986 by both the oil and dispersant treatments in all zones. In 1987, flowering shoot densities were high in the treated plots, particularly those in which heavy mortality in 1986 was followed by substantial vegetative recovery in 1987. This response was probably the result of a reduction of intraspecific competition which increased the proportion of resources available for flowering. Flowering shoot densities in the creek edge and midmarsh control plots declined in 1987, probably in response to drought conditions experienced during the 1987 growing season.

Total above-ground living biomass data for 1986 indicated that the midmarsh zone was severely affected by the oil treatments while the creek edge zone was virtually unaffected. Total above-ground living biomass in the high marsh zone was moderately reduced. Data for 1987 revealed full recovery for the creek edge zone. Total above-ground living biomass in the midmarsh zone increased significantly while recovery in the high marsh zone was rather poor. Total above-ground living biomass in the dispersant treated creek edge plots was significantly reduced in 1986 but returned to control levels by the end of the 1987 growing season.

Cover data collected during the 1986 growing season indicated little oil induced mortality in the creek edge zone, moderate mortality in the high marsh zone and severe mortality in the midmarsh zone. The dispersant treatment caused moderate mortality in the creek edge zone. Data from 1987 indicated little expansion of the Spartina sward in any of the zones. It was difficult to determine the degree of recovery in the creek edge zone since there was a considerable reduction in the cover of control plots between 1986 and 1987. It was impossible to determine whether the factor or factors responsible for the decline of the control cover would also act upon the treated plots. Drought conditions experienced in 1987 may have been responsible for the decline in control cover. Stress induced by the treatments may have been reduced during the 1987 growing season but was replaced by drought stress resulting in the lack of recovery noted in the various vegetation zones.

Annual halophytes such as Salicornia europaea, Suaeda maritima and Atriplex patula were rather rare in 1986. Oil and dispersant treatments generally resulted in reductions in their abundance during 1986. In 1987, large increases in the cover of these species were noted in the oil and dispersant treated plots. High negative correlation coefficients between the cover of the dominant Spartina species in each zone and the cover of these annual species suggested

that these species were rapidly colonizing areas where Spartina had been eliminated. Colonization was rapid in the creek edge zone but was relatively slow in the midmarsh and high marsh zones. In the midmarsh zone poor soil aeration and the physiological problems associated with it may have reduced the rate of colonization while in the high marsh zone the presence of a large standing crop of standing dead shoots may have reduced the rate of colonization of annuals through the shading of their seedlings.

This study has demonstrated that sensitivity to crude oil varies considerably among the various plant communities in the salt marsh. The creek edge zone, dominated by tall Spartina alterniflora was quite tolerant of the crude oil treatment. Results from 1986 reveal only small reductions in height, stem density, biomass and cover and by 1987 no evidence of toxic effects were apparant. Similar results have been found in several other studies (Delaune et al, 1979; Webb et al., 1981; Ferrel et al., 1984; and Webb and Alexander, 1985). The short Spartina alterniflora of the mid marsh zones, however, was very susceptible to the oil treatment. In 1986 all parameters investigated were negatively affected by the oil. In 1987 only limited recovery of this zone was noted. The stressful nature of the midmarsh zone predispose it to severe impacts from additional perturbations such as oil toxicity. In addition, the poor drainage of the zone reduces the rate at which the oil is flushed from the sediments or metabolized by microbes further contributing to the persistence of toxic effects in this zone. The impacts reported for the midmarsh zone illustrate the degree to which existing environmental stresses can affect the ability of a species or community to cope with pollutants.

The high marsh zone was intermediate in its response to the oil treatments. Most parameters demonstrated significant impacts in 1986, however, these impacts were not as catastrophic as observed in the midmarsh zone. Relatively little recovery was noted in the various parameters in 1987. This lack of recovery may be at least partially the result of the slow vegetative colonization of open patches and poor seed set which are normally associated with this species.

Exposure of the creek edge zone to the disperant resulted in considerably more damage than the crude oil. The toxic effects, however, were short lived and most parameters investigated in this study had returned to normal or were rapidly recovering one year after the disperant was applied. These results indicate that Corexit 9527 should not be used in close proximity to salt marshes.

All three vegetation zones demonstrated similar successional trends after exposure to crude oil. Annual species of Chenopodiaceae invaded the treated plots two years after oiling. Salicornia europaea and Suaeda maritima were the most important species. Their abundance

was inversely correlated with Spartina cover. We anticipate that the cover of these species will probably increase for two years following treatment, then decline as Spartina develops a dense sward. Based on current rates of recovery, the creek edge zone recovered from oiling within one year of treatment and will probably recover from the dispersant treatment within two years. The high marsh zone will probably require three to four years for full recovery, while the mid marsh zone will probably require at least five years.

The results suggest that lightly oiled marshes can recover relatively quickly. Natural cleaning may be ecologically preferred if oil contamination is low and/or when the oil enters only the creek edge zone. The use of relatively non-destructive clean up techniques such as low pressure flushing of the marsh surfaces may be justifiable if substantial portions of the midmarsh zone were oiled, provided trampling damage associated with the clean up technique was minimal. Oil induced damage to the high marsh zone, although significant, probably does not warrant the implementation of clean up techniques. The productivity of this zone was significantly reduced by exposure to the crude oil, however, the community structure of this zone remained intact and productivity can probably be expected to return to normal in a few years.

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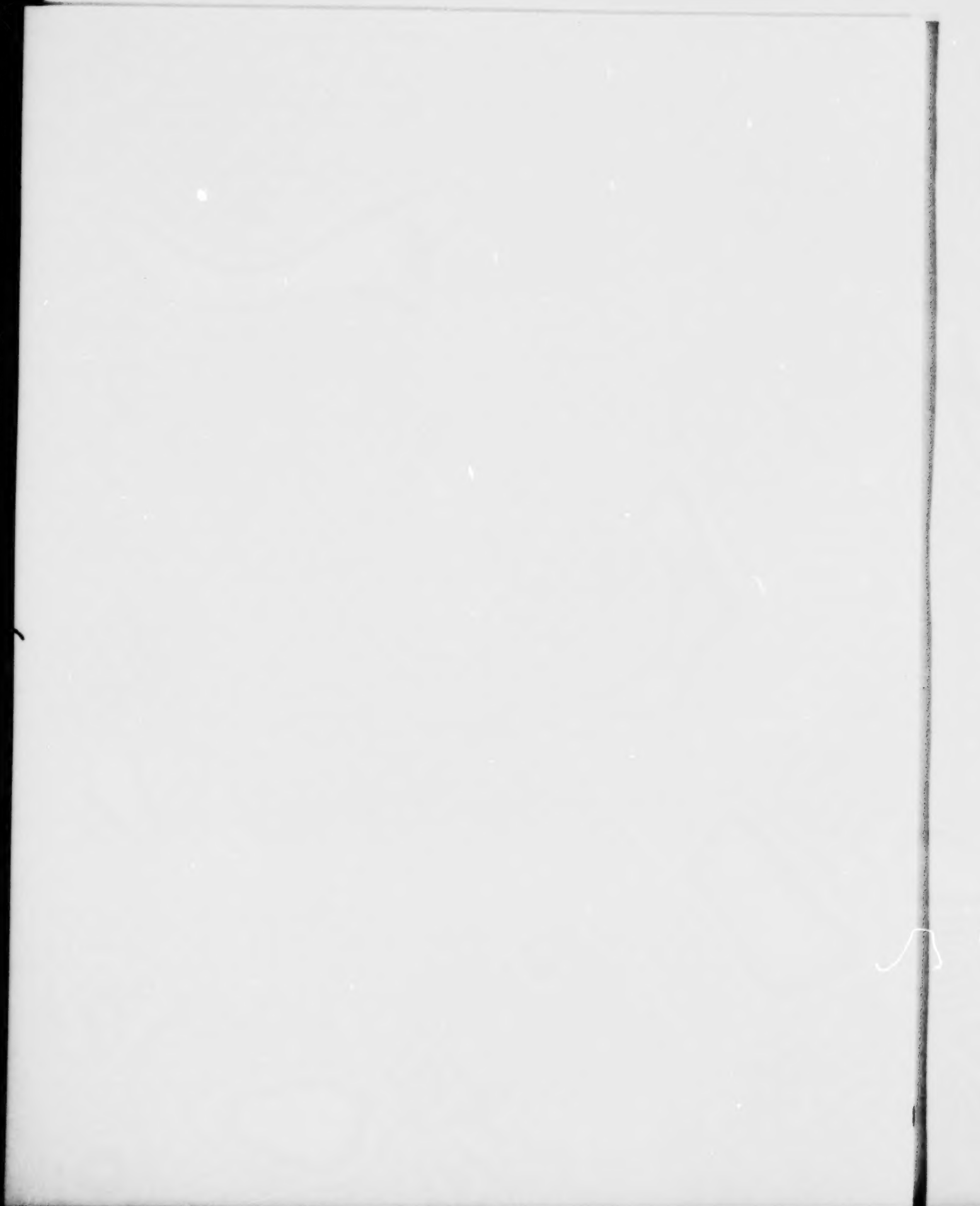
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BUBBLE BEHAVIOUR AT THE WELLHEAD OF A SUBSEA OILWELL BLOWOUT

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INTRODUCTION

Previous work on undersea blowouts and bubble plumes has indicated that the behaviour of the gas bubble very near the wellhead is of vital importance to the overall development of the bubble plume. For example, the fluid dynamic structure of blowout is normally immediately that of a plume rather than a jet because of the very quick bursting of the large bubbles formed at the wellhead (Rowe and Topham, 1982). This research concentrates on the formation, growth and departure of bubbles from the wellhead. The shattering of these large bubbles and the subsequent small bubble size distribution is also being studied. In addition, the flow distribution of the liquid in the vicinity of the wellhead is of interest. The information derived from this project is required to improve the prediction of the complex fluid flow phenomena near the wellhead of a possible subsea oilwell blowout with a view to deploying various devices to cap or at least contain the blowout (e.g. Brown and Root, 1985). Whilst the blowout is not capped or contained, the size distribution of the bubbles close to the wellhead is required to provide the lower boundary condition for free plume models (e.g. Laureshen and Rowe, 1987).

The study of bubble dynamics in liquids has historically been confined almost exclusively to rather small bubbles with diameters less than 1 cm. The physical forces governing bubble behaviour change drastically as bubble size increases: whereas small bubble dynamics are governed by surface tension and viscous forces, large bubble behaviour is governed by bouyancy and inertia. A review of the literature on bubbling from large diameter pipes (~ 10 cm) is provided in the next section of this paper; the diameters of these pipes are similar to those found in subsea oilwells. This is followed by a description of the apparatus that has been designed and build to study this problem. A numerical simulation of the flow distribution in the vicinity of large bubbles has been undertaken on a vector computer (Cyber 205); this work is reviewed in the last section of the paper. Good agreement has been found between these numerical results and the experimental data of Walters and Davidson (1962) for the sudden release of a large two-dimensional bubble from rest in a stagnant fluid.

LITERATURE REVIEW

A wide range of engineering applications exist in which the dynamics of bubbles are important. There is an abundance of literature investigating the effects of bubble size, surface tension, liquid viscosity, geometry of the bubble generating site, etc. (e.g. Clift, Grace and Weber, 1978). However, this literature is largely confined to small bubbles (<5mm diameter). As orifice size and gas flowrate increases, the amount of previous work declines. For bubbles in the size range of this research, it seems that only four papers exist. An indication of the type of work already done can be obtained by

constructing a parametric map of previous work; the two main parameters are chosen to be orifice diameter and volumetric flowrate. The work of these previous investigators can be mapped by indicating their run matrices on a log-log plot of these two parameters; such a map is given in Figure 1. Only a small number of the available studies for orifice diameter less than 10mm and gas flowrate less than 1 litre/sec have been included. Much work has been done in this region but it is of little interest to this research. To the authors knowledge, the map is complete for orifice diameters greater than 10mm and flowrates greater than 1 litre/sec. It should be noted that the boxes on Figure 1 only indicate the range of the two parameters for a particular study and do not guarantee complete coverage within the range.

Walters and Davidson (1962) considered a two-dimensional bubble and obtained the first analytical predictions of the distortion of large bubbles as they rise in a fluid. They supported their analysis with experiments on two-dimensional air bubbles suddenly released from rest in water. Their analysis was based on defining the velocity potential for flow around a cylindrical bubble. This velocity potential was an infinite series, with the first term being the well known potential for a cylinder in a uniform stream. The remaining terms of the series had time dependent coefficients. The basis of their method was to find expressions for these coefficients such that the condition of uniform pressure at the bubble surface would be satisfied. They found that the initial acceleration of a cylindrical bubble released from rest was g . Also, a tongue of fluid was found to penetrate the bottom of the bubble. Because of truncation of the infinite series defining the velocity potential, the analysis was only valid for small deviations from the cylindrical shape or until the bubble had moved about one bubble radius. Within this constraint excellent agreement with their experiments was found.

Walters and Davidson (1963) performed an important follow-up to this work by repeating their analysis for a three dimensional bubble. They performed similar experiments where a single spherical bubble was released from rest. Their analysis and experiments showed that such a bubble had an initial acceleration of $2g$. Again, a tongue of liquid penetrated the bottom of the bubble but did so much more rapidly than in the two-dimensional case. When the tongue of liquid reached the top of the bubble, the bubble broke into a spherical cap and a toroidal bubble with the toroidal bubble containing the vast majority of the original volume. Although this analysis was also restricted to small displacements from the spherical shape, the authors extended it to predict the time required for the tongue of liquid to contact the top of the bubble and the circulation produced upon break-up of the bubble.

In the same paper the authors also considered bubbles growing at submerged orifices. This is the portion of most interest to the current research. The above analysis was extended to a growing bubble by adding a source to the velocity potential. The analysis showed that the initial acceleration for growing bubbles was g . This was less than that obtained for a bubble suddenly released because the bubble could now acquire upward momentum through growth as well as acceleration. A detachment criteria was formulated based on the time required for the distorted bottom of the bubble to rise to the original site of the source. This expression predicted more frequent bubble departure than a spherical growth model because the upward deflection of the bottom of the bubble caused it to reach the source site sooner. However, they concluded that departure criteria models based on the spherical growth assumption were just as good because the effects modelled by

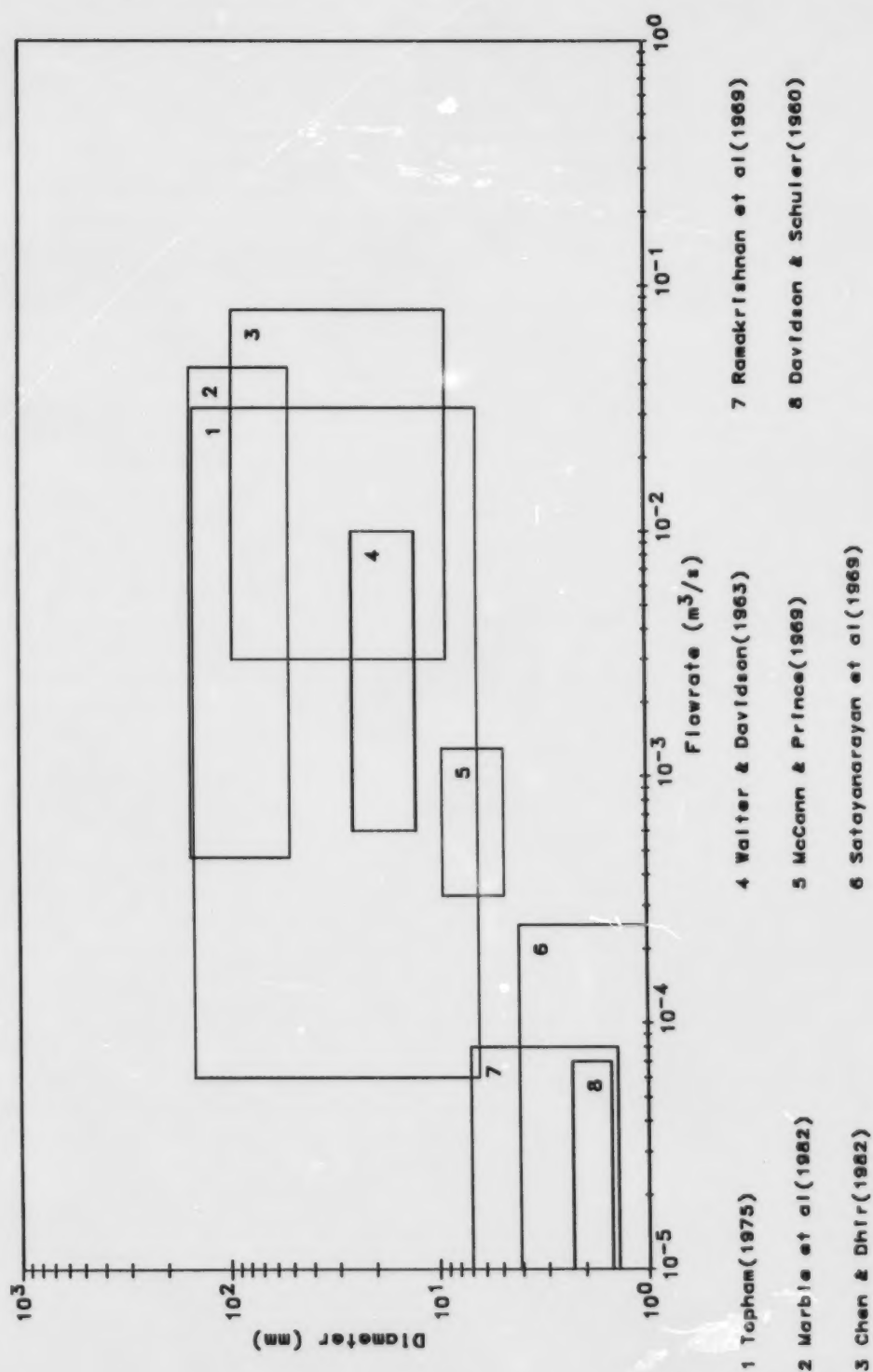


Fig 1 Parametric Map of Previous Work

the more sophisticated theory were masked by the presence of the orifice. The experiments looked at orifices of 13 to 25 mm diameter and flowrates of 0.6 to 10 litres/s.

Another work concerned with large bubbles and the one most directly related to the current study, is that of Topham (1975). He injected nitrogen into a 920 litre tank through orifices ranging from 0.64cm to 14.5cm at flowrates up to 32 litres/sec and stated that flow durations of 3 to 5 seconds were sufficient to establish stabilized flow patterns. He observed rounded bubbles growing from the orifice, releasing, and quickly bursting into smaller fragments. As the flowrate was increased the bubbles had a fluted surface appearance and the bursting was more violent. As the orifice diameter was increased the bubbles became flattened horizontally and breakaway was again characterized by violent bursting. No data concerning departure frequency or bubble size distribution after shattering were reported.

The work of Chen and Dhir (1982) was aimed at understanding the dynamics of a Boiling Water Reactor (BWR) pressure suppression pool when gas is injected into it through a downward facing pipe. Pipe diameters investigated were 0.9cm to 9.5cm with air flowrates of 3 to 80 litres/sec. A large part of their modelling effort was concerned with the vent clearing process. The pressure in the vent pipe rose almost to the gas supply pressure in order to accelerate the slug of liquid out of the vent. When the vent was clear and a bubble began to grow at the pipe outlet, the liquid inertia caused the initial growth rate to be higher than the air reservoir could maintain. This resulted in oscillations in bubble size and pressure which damped out within a few cycles. They observed that the bubbles start as discs and finally acquire a strawberry shape although the diameter/height ratio remained close to one during the final stages of growth. They did not discuss any departure criteria nor did they report the behavior of the bubble after departure. As a result, no data were reported on the size distribution of small bubbles upon shattering of the large bubbles.

Another paper dealing with BWR suppression pools is that of Marble et al. (1982). In considering the hydrodynamics of a large bubble rising in a pool they employed an energy balance to predict the size of the small bubbles upon shattering of the original bubble. They consider the potential energy of the original bubble (equal to the work required to submerge it) to be the initial energy available to the system. After rising some distance this energy is distributed among a population of smaller bubbles in the form of

- 1) the sum of the potential energy of the smaller bubbles,
- 2) the surface energy of the smaller bubbles,
- 3) the kinetic energy in the virtual mass of liquid travelling with the small bubbles,
- 4) the energy dissipated in the turbulent wakes of the small bubbles.

This simplified analysis predicts that the small bubble size will reach an asymptotic value very close to the point at which the large bubble is released (1 or 2 radii). If this quick change is considered to be the bubble shattering process, they have produced an expression to predict bubble size after shattering. Their work went on to experimentally study gas discharged from submerged horizontal vent pipes. They made no apparent attempt to verify their energy model with bubble size measurements from the tests but they did observe that large bubbles appeared to shatter within a short distance of being formed.

EXPERIMENTAL APPARATUS

The two main parameters to be varied in this study are pipe diameter and air flowrate. Other secondary variables that could be varied are fluid depth and distance between the pipe exit and the floor of the tank. It is proposed to vary the orifice size between 5cm and 15cm. The volumetric flowrate of air will be varied between 0.5 and 50 litres/sec. It is anticipated that several different regimes of behavior will take place within these ranges. These tests will use an existing 4' x 4' x 4' Plexiglas water tank developed for a related study (Rowe and Laureshen, 1988). This tank has been retrofitted so that pipes of various diameters and lengths can be mounted at the center of its floor. The apparatus required to deliver air to these pipes has been designed and built. It consists of a flowmeter section followed by a quick-acting bypass valve. The bypass valve discharges either to atmosphere or into a small plenum chamber mounted on the bottom of the tank. From there the air flows into the test pipes mounted on the floor of the tank.

It was decided to measure the air flowrate to the test pipe by means of a critical venturi meter. In addition to being quite accurate this type of flowmeter has the advantage of forcing a constant mass flowrate regardless of fluctuations in back pressure caused by bubble formation and departure. To select the desired flowrate for a test the air supply valve must be adjusted until the proper pressure is established upstream of the flowmeter. During this time the air should not be flowing into the water tank and generating bubbles. Therefore, a bypass system has been designed that will allow the air flow to be discharged to atmosphere while the proper flowrate is being established. Then the air can be suddenly diverted into the test pipe.

It is desirable to have axisymmetric velocity profiles at the test pipe exits. Since the test pipes are short (maximum 0.3 m), this is impossible to achieve through development length alone. It was therefore decided to install a small plenum chamber beneath the tank. Various sizes of test pipes could then be mounted on top of a common permanently installed plenum chamber and protrude up into the water tank. Flow from the plenum chamber into the test pipe is distributed in an axisymmetric fashion by a Mitsubishi flow conditioner mounted at the entrance to the test pipe (Akashi, Watanabe and Koga, 1979).

The main quantities to be measured in this work are as follows:

- 1) growth rate of initial bubble.
- 2) shape of the bubble as it grows.
- 3) volume of bubble upon departure.
- 4) rise velocity of bubble.
- 5) shape change of bubble after departure.
- 6) size distribution of small bubbles upon shattering.
- 7) fluid velocity in vicinity of orifice.

Most of the information listed above will be obtained by high speed photography. To obtain information about the flow pattern near the orifice while a large bubble is being produced, dye streams will be injected at various locations. To acquire more quantitative information about fluid velocities a laser Doppler anemometer system will be used to measure the velocity at several key locations within the tank.

NUMERICAL SIMULATION

The theoretical portion of this study consists largely of a numerical solution of the Navier-Stokes equations in the region near the exit of a large submerged pipe. The numerical solution of transient fluid flow with free boundaries is quite complicated; the main problem being the handling of the free boundary itself. The well known marker and cell (MAC) technique has proven to be a very successful method for such problems. The program that has been used here is the solution algorithm based on the concept of a fractional volume of fluid (SOLA-VOF), which is a refinement of the original MAC method. It can be used to study transient flow problems for a single fluid with free boundaries or two fluids with a density interface (Nichols, Hirt and Hotchkiss, 1980). It has a standard finite difference staggered grid common in fluid flow codes.

Large portions of the code have been converted to algorithms which are more suitable for the University of Calgary's Cyber 205 supercomputer. The original scalar version of the finite difference SOLA-VOF code had to be modified in order to apply vector techniques. The discontinuous nature of the flow field required extensive use of various masking, compression and expansion functions in order to vectorize the code. A sweeping tri-diagonal matrix algorithm has been used in place of the original Gauss-Seidel method. An overall speedup of about ten times has been achieved with these modifications. The details of these changes are provided in a paper to be presented at the Supercomputing Symposium '88 (Bugg and Rowe, 1988).

To date, only coarse grid solutions have been attempted; however, the results are quite encouraging. The first case to be presented is a two-dimensional bubble released from rest in a tranquil pool. This situation is intended to model an experiment performed by Walters and Davidson (1962). The field was divided onto a 30×80 uniform grid and the appropriate cells were initialized as being empty. The interior pressure in the bubble was set so that there was minimal tendency for the bubble volume to change upon release. Figure 2 shows the shape change of the bubble as time progresses. These are very close to the photographs taken by Walters and Davidson. Another check on the results is Figure 3 that shows the change of vertical bubble "diameter" D with time.

The second case is a submerged pipe outlet in a pool of water. At time $t = 0$ the pipe is full of air and there is no movement in the tank. However, there is slight overpressure in the pipe so that as time progresses a bubble begins to form at the pipe exit. A typical time sequence of such an event is shown Figure 4. These solutions are based on a 18×24 grid. The bubble grows from the pipe exit until it reaches a certain size. It then departs and rises on its own as a new bubble begins to form. The pressure in the pipe is constant but once the bubble has departed it is assumed to contain a mass of air that will behave isentropically. Therefore, its pressure is adjusted after each time step according to its change in volume.

ACKNOWLEDGEMENT

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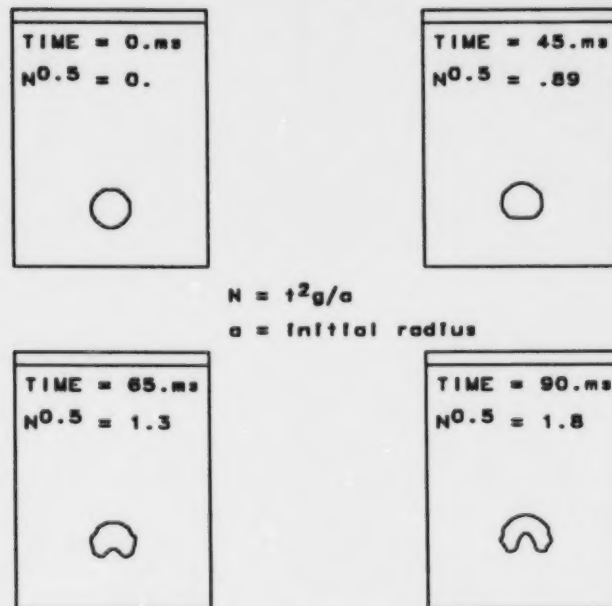


Fig 2 Two-Dimensional Bubble Rising

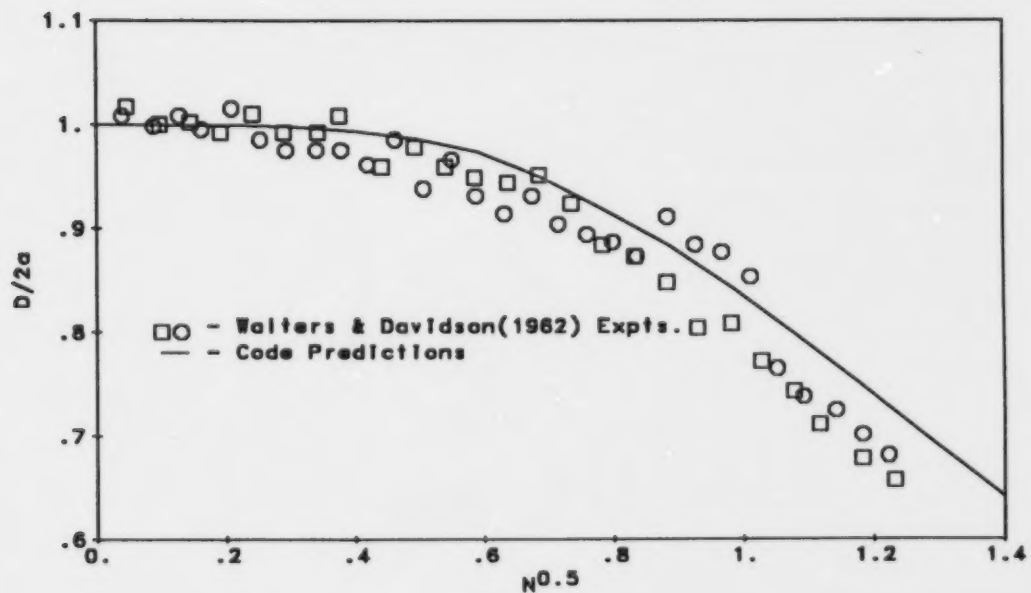


Fig 3 Vertical Bubble Diameter vs Time

Pipe Diameter = 10 cm
 Pressure in Pipe = 3433.5 Pa
 Hydrostatic Pressure at Pipe Exit = 3399.2 Pa

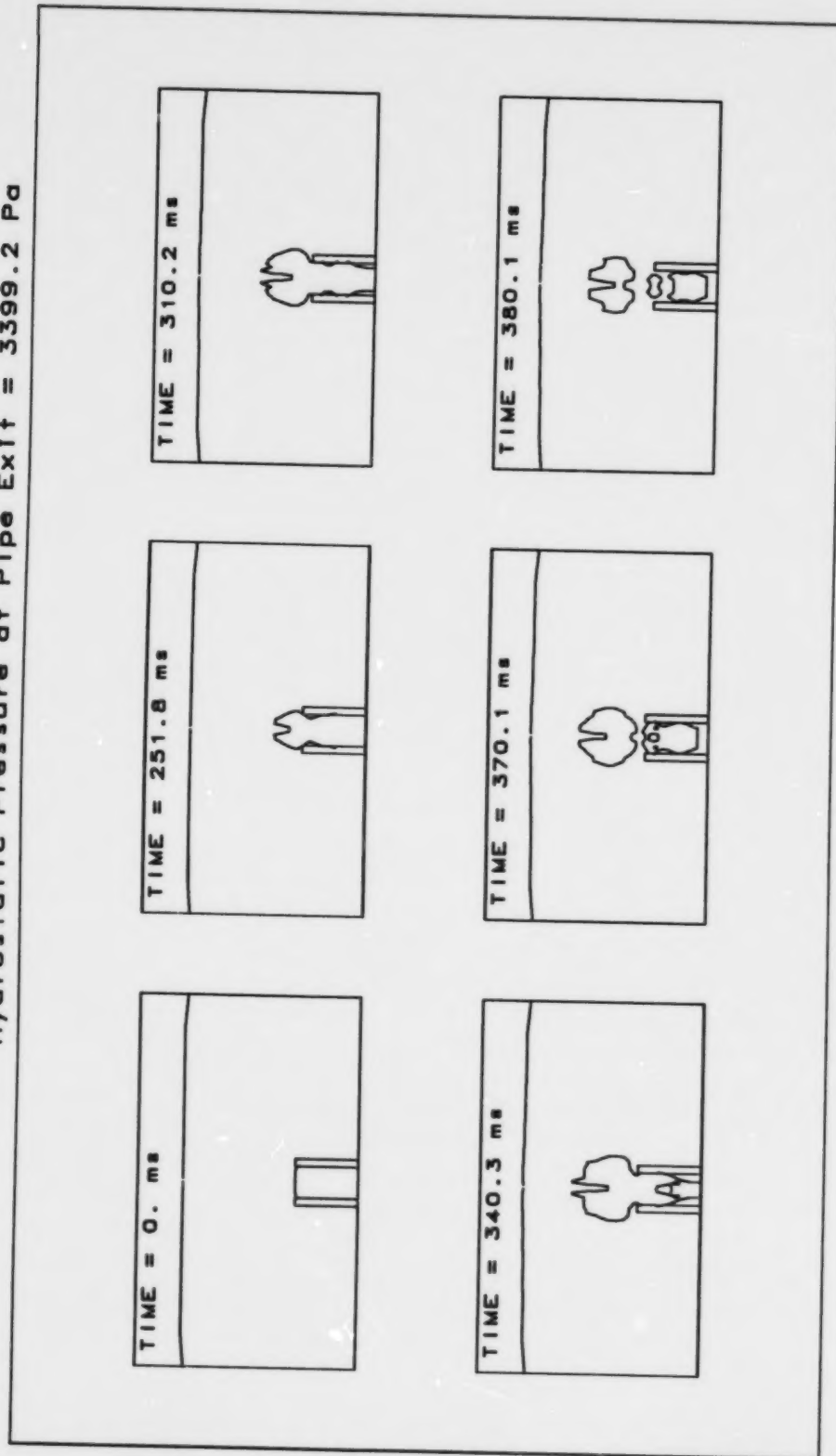


Fig 4 Large Bubble Simulation

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**A MICROCOMPUTER-BASED SPILL IMPACT MODEL
AND ITS APPLICATION TO OIL SPILL DISPERSANT USE
DECISION-MAKING IN THE U.S. GULF OF MEXICO**

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INTRODUCTION

In responding to a marine oil spill, the first priority of the response team is to remove oil from the sea and eliminate the environmental risk. However, in some situations, collection of oil is difficult if not impossible and chemical dispersants may be used to decrease the overall impact of the spill. Unlike physical recovery techniques, treatment of oil spills by dispersants does not remove oil from the sea but only moves it from the surface into the water-column. Although this eliminates the hazard to surface dwellers (sea birds, mammals) and to shorelines, it increases the threat to water column and benthic resources.

In making a dispersant decision, decision-makers are faced with two problems. First, they must determine logically and objectively whether the effects of the oil and dispersants on water-column resources will be significantly less than effects of the untreated oil on surface dwellers. Second, they must make their decision very quickly since dispersants are not effective on oils that have weathered on the water surface and become viscous. Unfortunately, the procedure for predicting spill effects can be complex and lengthy. Clearly, methods are required to simplify and speed up the impact assessment procedure.

In recent years S.L. Ross has been involved in developing spill impact assessment methods and rapid, rational, real-time methods for dispersant decision-making. The present paper describes a user-friendly, microcomputer-based, spill impact assessment model that is nearing completion and its application to the problems of dispersant decision-making in the U.S. Gulf of Mexico.

DISPERSANT DECISION SYSTEM

Dispersant decisions hinge on three major interacting considerations:

- i) effectiveness of available dispersants against the type of oil spilled;
- ii) capacity of available equipment to treat the volume of oil spilled under prevailing spill conditions; and
- iii) trade-off of reducing the impact of untreated oil on certain resources against increasing the impact of the spill on other resources if dispersants are used.

The prevailing consensus is that questions of dispersant effectiveness and logistics limitations are amenable to straight forward analysis in real-time or during planning, however environmental trade-offs are far more complex and require development of a general formula for decision making and a simple, rapid method of making necessary computations in real-time.

In general, it has always been felt that dispersants should be used only in situations in which their use would significantly reduce overall impact of a given spill. However, demonstrating this significant reduction in impact posed certain problems.

1. How can effects of dispersed oil on finfish be computed and compared with effects of untreated oil on birds or on oil-sensitive habitat that they both depend on?
2. How does one take into account differential sensitivity, vulnerability, and recovery potential of vastly different kinds of resources?
3. How to take into account differences in value or importance of different resources?
4. How to take into account the possible tactical use of other countermeasures to protect highly important, threatened resources.

In order to deal with these questions and concerns, a formula was developed in which consideration could be dealt with in a logical systematic way. This formula is outlined in the flow chart in Figure 1.

For any given spill, the decision-maker considers two principal courses of action, disperse or no disperse. For each alternative, the potential spill impact is computed on a wide variety of oil-sensitive and oil-vulnerable resources including representatives from each of the following groups: habitat (marsh, seagrass); benthic, demersal, and pelagic fin- and shellfish; birds; mammals; reptiles; shorelines; and property. Impact estimates for the untreated and chemically-dispersed spill are then compared and analysed to determine the alternative which yields the lesser overall environmental impact. The decision-maker then considers other factors such as the relative value or importance of the affected resources or the possible tactical use of alternative countermeasures to protect critical resources to determine whether these factors will influence the decision. Once these factors have been considered the decision-maker is in a position to formulate a final decision on the merits of dispersant use.

A key component of this decision-making system is the impact or damage assessment model. This model is described in more detail in the following paragraphs.

Impact Assessment Model

The algorithms used in the impact assessment model compute proportions of populations or stocks of individual species that are at risk from the spill. Algorithms are based on methods developed in Trudel et al. (1986) which have been tested and refined in workshops in a variety of environments. However, unique detailed algorithms have been developed for each of the 70 resources of the Gulf of Mexico study to take into account unique aspects of these resources.

The general structure of the algorithms is illustrated in Figure 2 using the white shrimp, *Penaeus setiferus*, algorithm as an example. Spill conditions are input by the user, an oil fate model and toxicity criteria are used to compute areas of effect for the various sources of damage that might befall white shrimp populations or fisheries. The system computes the proportions of the various shrimp populations that might be affected by the spill, the proportional reduction in the annual yield to the white shrimp fishery that might result from damage to white shrimp stocks, and the disruptive effects of the spill on fishing activity. Several aspects of the impact assessment algorithm are discussed in detail below.

Spill Conditions Information on spill conditions is input by the user using a menu system. The user specifies the type and volume of oil spilled, spill location and date, whether or not dispersants are used and the time of dispersant application. The user also enters forecast wind data by specifying wind speed, direction, and interval duration for an unlimited number of intervals over the period of the spill.

Oil Fate The oil fate routine is used to compute oil movements, spreading of oil slicks and oil clouds and concentrations of oil on the surface and in the water column to which organisms may be exposed. For this application we have used an in-house oil fate model based on the work of Mackay and Leinonen (1977). The system accounts for all major oil spill processes including advection, spreading, evaporation, natural dispersion, and emulsification. Properties of the appropriate oil are read from files, and data on local ocean currents are obtained from the maps held in the geographic information system (GIS). The system generates areas, locations, and thicknesses of slicks, oil properties, and oil concentrations in the water-column as a function of time after the discharge. This oil fate model has been verified by comparison with existing data for behaviour of major spills.

Oil fate output is in the form of a GIS-based map showing the size and location of oil slicks and oil clouds at various times after the spill, as well as, ecotoxicologically-relevant data such as slick thickness and oil concentration in dispersed oil clouds.

Areas of Effect The size and location of areas of effect (AOE) are estimated by determining the size and location of oil slicks and oil clouds at the point at which conditions within the slick cloud fall below threshold values for effects on resources. Since different resources have different sensitivities to oil, AOE's are estimated for a variety of resources. In the case of the white shrimp the following AOE's are defined:

- i) areas within which hydrocarbon concentrations are lethal to larvae and postlarvae;
- ii) areas within which hydrocarbon concentrations are lethal to juveniles and adults;
- iii) areas within which hydrocarbon concentrations are sufficient to cause tainting; and
- iv) areas within which surface oil concentrations are sufficient to interfere with fishing activity.

Toxicity threshold values used in determining AOE's were derived from published toxicity studies in which exposure conditions in tests were roughly similar to real-world exposure conditions and in which oil concentrations in tests were measured.

Biological Effects This segment of the program computes proportions of populations of each species that are at risk from the spill by estimating the proportion of standing crops that lie within the AOE and correcting for seasonality and vertical distribution of the target species. Since, in many species, life stages differ in their habitat use, habits, and sensitivity to oil, the effects on different life stages are computed separately and are then combined to yield overall population effects.

The proportion of the standing crop of a life stage that is at risk from the spill is determined by using the analytical power of the GIS to overlay the AOE map for the appropriate life stage on its distribution map and then computing the proportion of the population that lies within the AOE. This has traditionally been the most difficult and time consuming aspect of the impact calculation, but this task has been greatly facilitated through the use of the SPANS geographic information system. The SPANS system accepts output from the oil fate model and using data on toxicity thresholds creates maps of the AOE's. The AOE map is then overlain on a map of the distribution of the relevant resource life stage. An example of a resource map

showing the summer distribution of white shrimp larvae and postlarvae is in Figure 1. This map shows the limits of distribution of different white shrimp populations. The general geographic distribution of the species was taken from a recently published extensively reviewed source, NOAA (1985). Where possible, the breakdown of resources into stocks was accomplished using traditional resource management sources. The location of areas of higher concentrations of resources and the degree of aggregation were determined from published large scale surveys. Since population densities vary widely from year to year, resource densities are expressed in terms of relative concentrations (e.g., 25x, 4x, .1x). Since resource distribution vary seasonally, unique distribution maps have been developed for different times of the year for all life stages of all resources as far as the data would permit. Data on timing of the seasonal cycle of spawning and development and vertical distribution of life stages in the water column are input from files and are used to conduct impact estimates for seasonality and vertical distribution.

Impact estimates are output directly (Table 1) and are also used as input into the fishery impact model.

Fishery Effects Effects of the spill on fisheries are expressed as the proportional reduction in annual fishery yield that might occur as a result of the spill. Three sources of damage are considered: 1) damage to the white shrimp populations(s) that support the fishery; 2) short term closure of the fishery that might result from tainting or the threat of tainting by naturally dispersed or chemically dispersed oil; and 3) short term exclusion of the fishing fleet from the spill area due to the presence of an oil slick.

Effects on fisheries resulting from damage to the shrimp stocks are computed using the estimated reduction in stock size computed in the "Biological Effects" part of the algorithm. This value is corrected for the proportion of the annual yield that is supplied by that stock, and the proportion of the annual catch remaining to be taken at the time of year in which the spill occurs. These data are read from files.

Computation of effects of oil slicks on fishing activity assumes that if a visible oil slick is present, fishermen will avoid the contaminated area due to the threat of gear or catch contamination or due to the existence of a navigation exclusion zone in force in the area of the slick. The proportion of the catch affected is estimated as the proportion of the fishing area that is overlain by the slick. Since certain parts of the fishing area yield greater catches than others, different parts of the fishing area are weighted more heavily than others. To do this fishing areas are divided into zones corresponding to the National Marine Fishery Service commercial fishery statistical zones. Zones are weighted according to the mean proportion of the catch taken in each zone as per NMFS commercial catch data for 1983-1985 (Figure 4). Since fishing activity also varies seasonally, the proportional effect on the fishery is also weighted in terms of the proportion of the annual catch historically taken at the time of year of the spill.

Computation of possible effects of tainting on the fishery are computed in roughly the same way as are the fishing activity effects. However, since tainting or even the threat of tainting may effect the value or marketability of the catch taken over an area larger than that of the immediate area of the spill it is assumed that the entire catch from the fishery statistical zone is lost for the month of the spill.

The net effect of the spill on the fishery is taken to be the sum of the biological effects and either the fishing activity effects or the tainting effects which ever is greater.

Output The results of these computations are output in two forms. Values for proportional effects on populations and fisheries are output along with computed effects on all other resources in a summary table (Table 1). This table is designed to be used by decision-makers to formulate their decision. A detailed summary of the computations of effects on individual species is output in a second table that decision-makers may refer to if additional data are needed in verifying the predicted impact.

Key Resources in Gulf of Mexico Study

Most marine environments contain hundreds or even thousands of resources and it is impossible to try to compute effects on all of them. It is possible to consider only the most ecologically or economically important resources that are oil-sensitive and oil-vulnerable. Care must be taken in selecting resources to be included in the study to ensure that the selected resources represent an environmental cross-section of the area under study and that bias is avoided in the selection progress. For example, if only shoreline resources, marshes and mangroves are included, then estimates of impact will always favour the use of dispersants since untreated oil will always present the greater hazard.

The short list of important resources in the Gulf of Mexico was developed as follows. First, resource groups that have been shown historically to be sensitive to oil were identified. These included the eight categories of invertebrates, finfish, birds, mammals, reptiles, biologically sensitive habitat, shorelines, and property. A preliminary list of about 200 major Gulf resources in these categories was then compiled. A team of resource experts representing each of the states involved was charged with the responsibility of reducing this to a workable number. A final list of 70 resources was developed. These included endangered species and resources that are of major importance from an economic or ecological point of view. Model species were included that are representative of groups occupying different habitat types such as shorelines, estuaries, nearshore, shelf and open ocean. For groups of species of similar habits, one or two model species were selected to represent each group. Because the very large study area cut across several biogeographic provinces, it was necessary to include representatives of major groups from each biogeographic area. Habitat types and species of unique, local importance were also included. When all of the above factors were considered, the list of biological resources that appears in Table 2 was developed. Also included in the study but not shown in the table were certain property resources and all shorelines in the study area.

Table 1

Impact summary for dispersed and untreated
spill occurring off Charlotte Harbour, Florida
(Southwest Florida) .

Spill conditions: – 10,000 m³ light crude
 – June
 – winds, constant west at 10 km/h
 – location, 82.6°W 26.4°N

Resources	Spill Impact ^{2,3}	
	Untreated	Dispersed
Shrimp, White [5] ¹	0.3 (0.6)	0.9 (1.6)
Snapper, Mangrove [5]	0.6 (1.2)	2.5 (3.6)
Mackerel, Spanish [2]	0.1 (0.1)	0.7 (0.3)
Seatrout, Spotted [6]	2.0 (2.6)	2.8 (3.3)
Tern, Least [2]	12.0	0
Pelican, Brown [2]	3.5	0
Manatee [2]	1.8	0
Mangrove, Habitat [4]	8.9	0
Marinas ⁴	23	0
<u>Shorelines⁵</u>		
Beach, Non-Amenity	64.0 km	0
Mangrove	11.5 km	0
Mean shoreline dose	11.5 l/m	0

1. Value in square parenthesis indicates specific population affected.
2. Impact estimates expressed as percent affected.
3. Values in parenthesis represents effect on fisheries.
4. Impact on marinas indicates number of marinas oiled.
5. Shoreline contamination expressed as length of shoreline oiled in km.

TABLE 2
BIOLOGICAL RESOURCES INCLUDED IN THE
GULF OF MEXICO DISPERSANT STUDY

HABITATS

salt marsh
 mangroves
 seagrass
 coral reefs
 oyster reef

REPTILES

green seaturtle
 loggerhead seaturtle
 Kemp's ridley seaturtle
 leatherback seaturtle
 American crocodile
 gulf saltmarsh snake

MAMMALS

manatee
 right whale

INVERTEBRATES

brown shrimp
 pink shrimp
 white shrimp
 blue crab
 stone crab
 spiny lobster
 eastern oyster
 mercenaria clam
 bay scallop
 queen conch

BIRDS

lesser scaup
 mottled duck
 redhead duck
 common loon
 laughing gull
 royal tern
 least tern
 sooty tern
 black skimmer
 reddish egret
 snowy egret
 great white heron
 sanderling
 piping plover
 snowy plover
 oystercatcher
 northern gannet
 magnificent frigatebird
 brown pelican
 whooping crane
 roseate spoonbill
 bald eagle
 osprey

FINFISH

bay anchovy
 gulf menhaden
 spotted seatrout
 black drum
 red drum
 southern kingfish
 striped mullet
 sheepshead
 tarpon
 snook
 southern flounder
 spanish mackerel
 king mackerel
 cobia
 crevalle jack
 Florida pompano
 Atlantic croaker
 red snapper
 mangrove snapper
 scamp grouper
 sailfish
 sturgeon
 sand seatrout

Computerization of the Impact Assessment System

The main objective of the Gulf of Mexico dispersant project was to identify dispersant use/non-use areas in the Gulf by analysing a large number of spill scenarios using the workbook system (Trudel et al. 1986).

Concerned with the tedium and time demands of doing hundreds or even thousands of such analyses by hand, the first task in the project was to determine how these area analyses could be done by computer mapping. After a review of the market, a unique software package developed by Tydac Technologies Inc. (SPANS or Spatial Analysis System) was identified as being appropriate for our needs.

The SPANS software operates under MS-DOS on PC compatible micro computers but retains a degree of sophistication in data input and analysis normally found only on mini computer or mainframe geographical information systems (GIS). In many cases analytical capabilities of SPANS exceed those of much larger systems that have been designed primarily for data input and display. The hierarchical quadtree data structure implemented by Tydac is becoming recognized in the GIS industry as one of the most efficient. This data structure reduces file storage space, reduces the number of calculations needed to manipulate data and also permits maps prepared at different levels of resolution to be analysed in overlays without translation to the poorest resolution in the map set.

By developing our automated environmental impact decision-making system around a personal computer system, the end product is much more portable and accessible to potential users.

To facilitate the use of the oil fate model in the computer system, the program has been coupled directly to Tydac's SPANS software such that it generates a data output file that converts directly to a map file for final impact analysis. This integration also permits water currents in the vicinity of the spill to be taken directly from a SPANS format current map for use in trajectory analysis during the modelling session.

At present, to estimate the effects of a treated or untreated spill, the user simply selects an oil type (heavy, medium or light crude), a spill volume, a spill location (by longitude and latitude), the time of year of the spill (by month, to establish which water currents prevail), and the winds that will affect the fate and movement of the slick (speeds, directions and durations). The system then maps the resulting oil fate predictions including the important slick attributes (thickness, dispersed oil concentration etc.). The resulting oil map is then automatically overlain onto the resource maps to determine overlap areas involving critical oil concentrations for each of the resources. The final output from the program is a list of quantitative impact values for each of the species populations that are affected by the oil. The outputs from treated and untreated spills can then be compared to arrive at a final dispersant-use decision.

Preliminary indications are that it will take less than one hour to produce a fully documented impact assessment and dispersant decision for a spill in the Gulf involving the 70 key resources.

STATUS OF THE STUDY

At present the project is nearing completion. The fully operational user-friendly impact assessment system has been developed, tested, and reviewed by end-users. The data base containing forty-five of the seventy resources has been assembled and loaded into the system. Completion of the database, final testing, and revision of the system will be completed in time for delivery in the fall of 1988.

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FIGURE 1
GENERAL FORMAT FOR ENVIRONMENTALLY-RATIONAL
DISPERSANT DECISION-MAKING

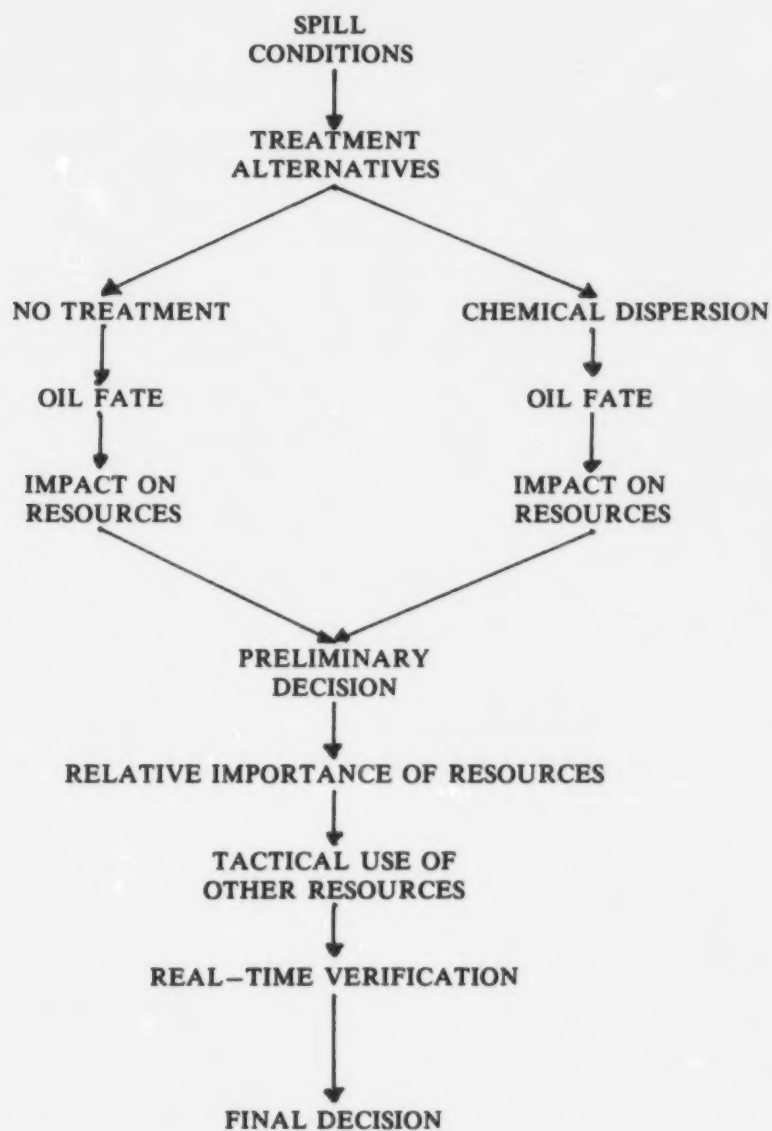


FIGURE 2

**ALGORITHM FOR COMPUTING EFFECTS OF DISPERSED OR
UNTREATED OIL ON WHITE SHRIMP STOCKS
AND ASSOCIATED FISHERIES**

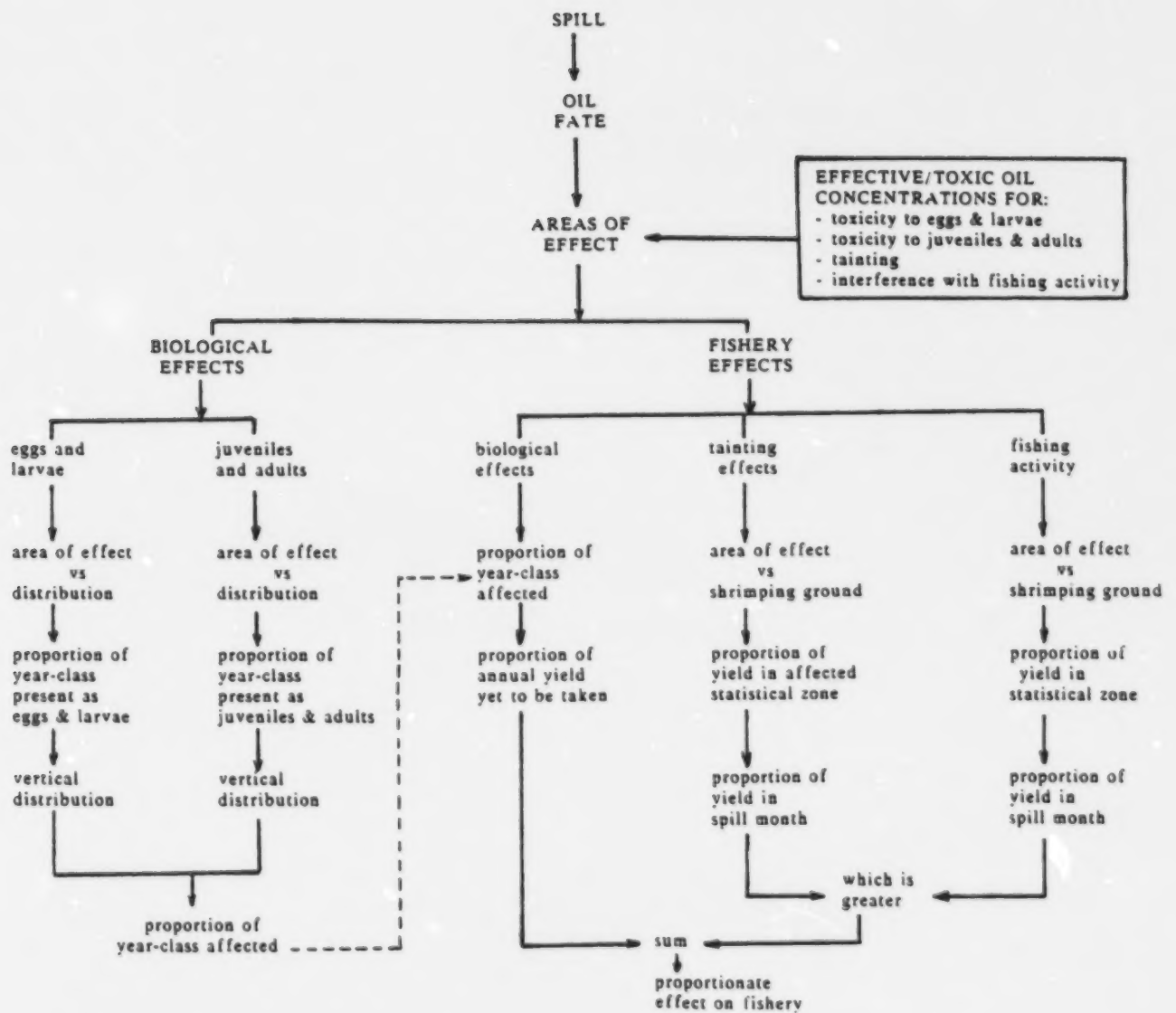


FIGURE 3

**DISTRIBUTION MAP FOR LARVAE OF WHITE SHRIMP
POPULATIONS IN THE GULF OF MEXICO STUDY AREA, JULY-OCTOBER**

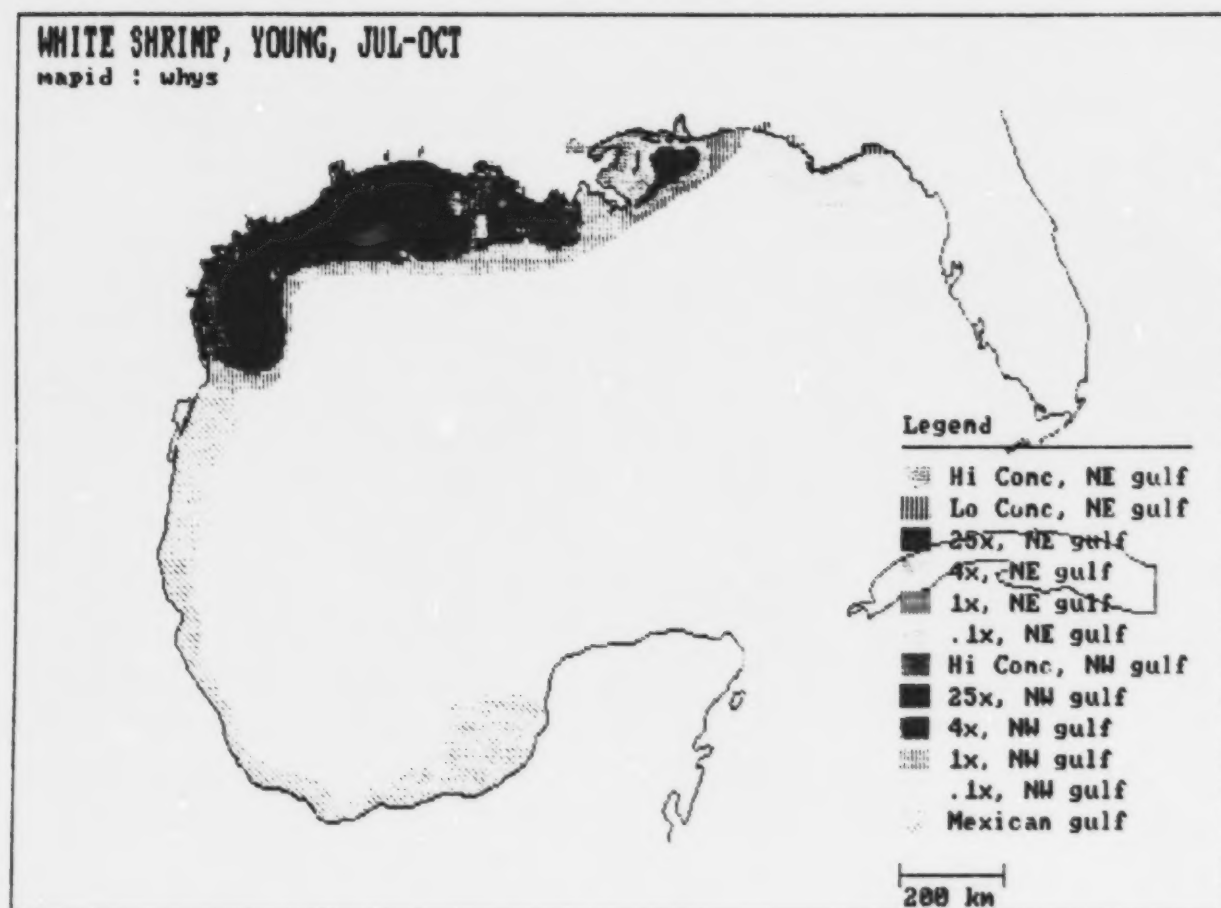
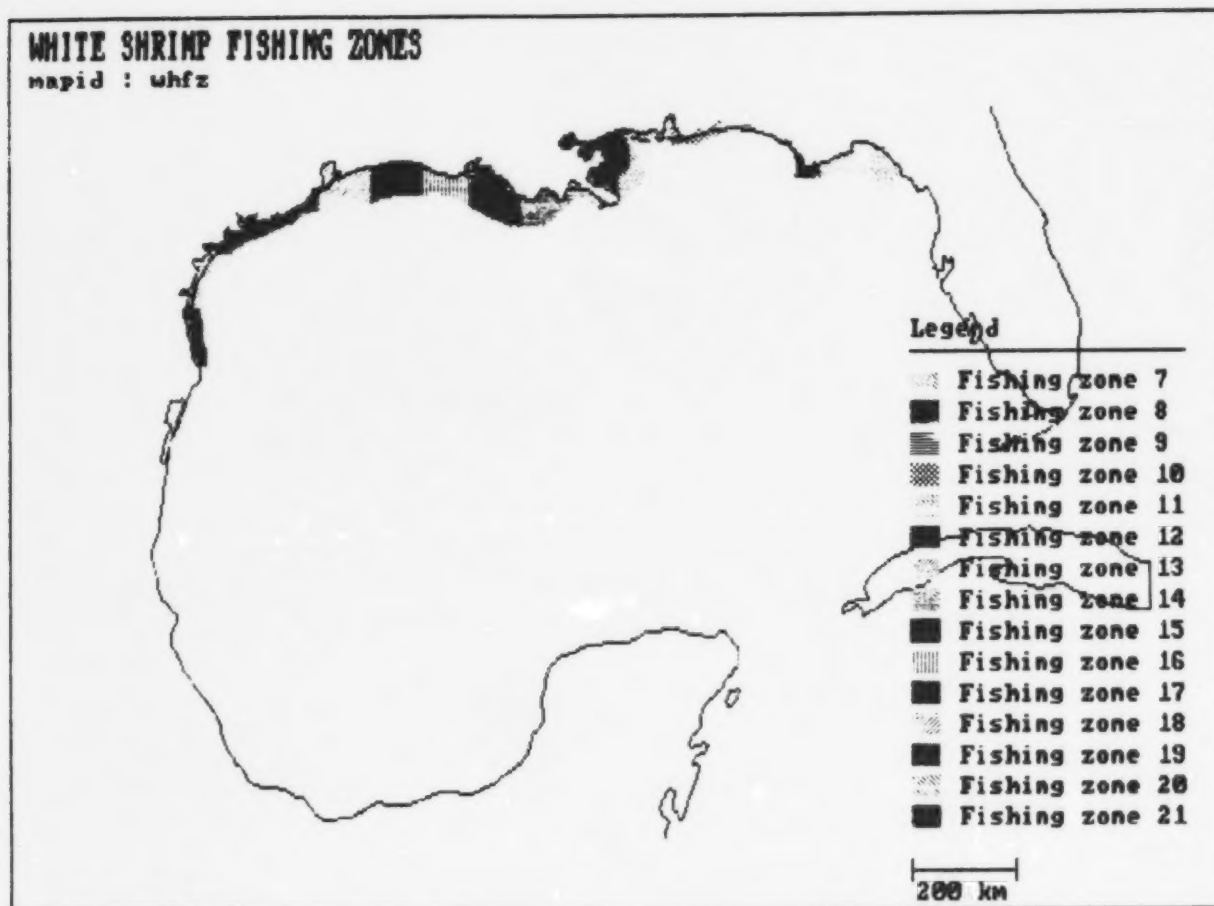


FIGURE 4

DISTRIBUTION MAP OF WHITE SHRIMP FISHING ACTIVITY
WITHIN THE GULF OF MEXICO STUDY AREA





A STUDY OF THE FORMATION AND STABILITY OF WATER-IN-OIL EMULSIONS

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BACKGROUND

The study presented in this paper is part of a three year research program called DIWO ("Application of Dispersants on Weathered Oils") presently running at IKU. The main objectives in this research program are:

- * to determine the "relative" dispersability of oils produced or transported in Norwegian coastal waters. Particular emphasis is placed on the effect of weathering of the oil on dispersant effectiveness and to elucidate the "time window" for dispersion of the different oils.
- * to study the formation and stability of w/o-emulsions as a function of type of oil and degree of weathering.
- * to develop new dispersants with high performance on weathered oils.

This paper deals with the preliminary results of the w/o-emulsion formation and stability study performed on three crudes in the first part of the DIWO program. The preliminary results of the chemical dispersability study in the DIWO program are presented elsewhere in this volume (Daling, 1988).

INTRODUCTION

Water-in-oil emulsion (w/o-emulsion) or "chocolate mousse" is more poorly understood than the other weathering processes of oil at sea although extensive studies have been performed in recent years (e.g. Bridié et al., 1980; Mackay and Zagorski, 1982; Ross, 1986). Excellent literature reviews on this subject are available in Payne and Phillips (1985) and Mackay (1987).

A w/o-emulsion is a highly viscous oil spill product often composed of over 80 percent water. The water is in the form of μm -sized droplets dispersed and tightly bound in a continuous phase of oil. The w/o-emulsions can have viscosities several hundred times greater than that of the parent oil. It is obvious that once a surface oil spill is converted into such a stable, viscous w/o-emulsion, its chances of being broken up and dispersed either by natural wave action or by chemical treatment are greatly reduced.

The physico-chemical properties of an oil have a pronounced effect both on the formation tendency and stability of the w/o-emulsion. W/o-emulsions are probably stabilized by colloidal particles (e.g. asphaltenes and waxes) which gather at the w/o interface where they may form a stable film of considerable mechanical and elastic strength around the water droplets. Possible mechanisms of formation and stabilization are postulated and discussed by Mackay (1987).

The tendency for crude oil slicks to form w/o-emulsions on the sea surface results in substantial changes in behaviour, and effects and necessitates changes in countermeasure approaches. It is therefore desirable to understand, as fully as possible, the factors which cause an oil to emulsify, the rate at which the emulsification occurs and the w/o-emulsion stability of a given oil under given environmental conditions. The influence of other weathering processes (e.g. evaporation and photolysis) are especially important for the properties of the w/o-emulsions formed.

Finally, the effectiveness of chemical treatment on different w/o-emulsions qualities is also poorly understood. Demulsifiers are used to "break" w/o-emulsions (to separate the water from the oil) either during in-situ treatment on the sea surface or on mechanically recovered w/o-emulsions. W/o-emulsion inhibitors are added in small amounts to fresh oil to inhibit or retard w/o-emulsification, thereby enhancing the dispersion of the oil by natural sea turbulence. Recent studies (e.g. Ross, 1986; Lichtenhaler and Daling, 1985) have showed that certain oil spill dispersants may act both as w/o-emulsion breakers and as w/o-emulsion inhibitors.

OBJECTIVES

The main objectives of the study presented in this paper have been to study:

- * the rate of w/o-emulsion formation
- * the maximum water content in w/o-emulsion
- * the stability of w/o-emulsions (untreated and treated with a dispersant concentrate)
- * the w/o-emulsion inhibition effectiveness of a dispersant concentrate

These processes have been studied as functions of type of crude, mixing time, temperature and weathering (evaporation, photolysis).

EXPERIMENTAL

Test method

Principle. The method used for this w/o-emulsion study is based on the rotating flask method of Mackay and Zagorski (1982). The principle of the method is to rotate centrifuge bottles containing sea water and oil for a fixed period of time at a defined rotation speed. After the mixing period, both the formation tendency and stability of w/o-emulsions formed are assessed. Some modifications have been made to the original procedure by Mackay and Zagorsky (1982) for the present study. The shape of the centrifuge bottles is somewhat different: The total volume of the flasks is 55 ml (internal diameter: 25 mm, height: 115mm). Figure 1 shows the bottles used.

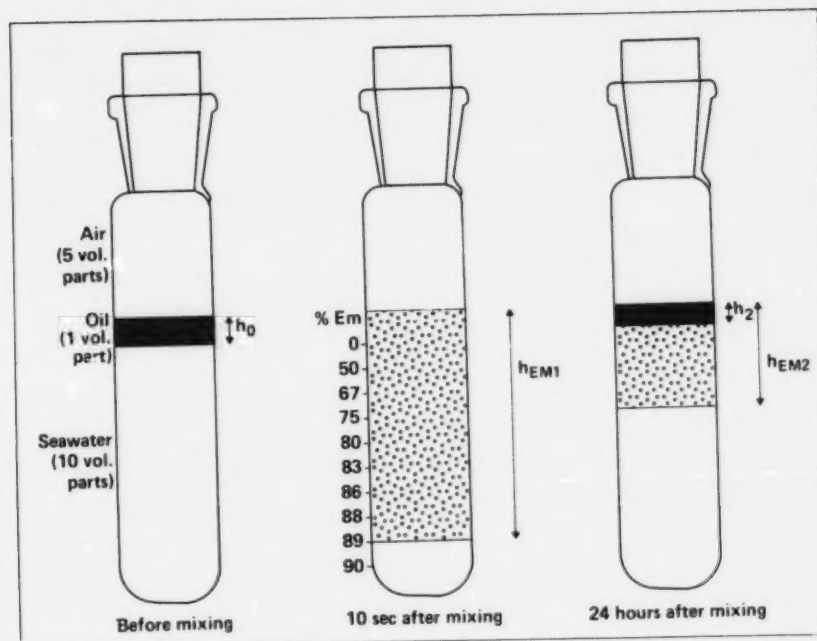


Figure 1. Schematic of the rotating bottles used in this study.

Test condition. The experiments were performed under the following condition:

Volume ratios : 35 ml water / 3.5 ml oil / 16.5 ml air (W:O:A = 10:1:5)

Rotation : 63 (+/- 2) rpm.

Mixing time : 1 and 24 hours.

Temperature : 6 and 13°C (North sea winter and summer condition).

The bottles containing the oil and seawater were conditioned at the test temperature for at least 1 hour before the mixing process. This paper deals mainly with the results of the 13°C tests.

Parameter definitions. After the mixing period, the w/o-emulsion formation tendencies and w/o-emulsion stabilities were determined by observing the location of both the oil/emulsion interface and the emulsion/water interface. Because of the fact that the diameter of the bottle is constant, the volume fraction is proportional to the height.

The following parameters were used to evaluate the formation and stability of the w/o-emulsions:

$$\%EM = ((h_{EM} - h_0)/h_{EM})100\%$$

$$R = (h_{EM} - h_0)/h_0$$

WEM: the volume percent of water in the w/o-emulsion
R : the volume water-to-oil ratio in the w/o-emulsion

WEM₁: Initial water content: defined as the vol.% of water in the w/o-emulsion immediately (10 sec) after mixing.

R₁ : Initial water-to-oil ratio: defined as water-to-oil ratio in the w/o-emulsion immediately (10 sec) after mixing.

R₂ : Water-to-oil ratio at infinite time: defined as water-to-oil ratio in the w/o-emulsion/oil mixture 24 hours after mixing.

R_{2/1}: Relative water-to-oil ratio: defined as the R₂-value divided by the R₁-value.

Oils used in the study

The w/o-emulsion tests were performed on topped and photolysed oil fractions of the following crudes: Gullfaks crude, Statfjord crude and Arabian Heavy crude. Each crude was topped at 150°C, 200°C and 250°C (vapor temperature, ASTM-method D86/82). In addition fresh crudes were photolysed for 1.5 and 20 hours. This photolysis caused an evaporative loss of the lightest oil components which was similar to the 200°C+ and 250°C+ topped fractions. The procedures for the topping and photolysis are given by Daling and Almås, (1988).

Type of experiments

This study includes the following type of experiments:

1. Rate studies of w/o-emulsions formation. In these tests the rate of water uptake in the oils was followed by measuring the WEM-values during a 24 hours mixing period at the following times: 0.25, 0.5, 0.75, 1, 2, 4, 6, 8, 10 and 24 hours from the start of the mixing.

2. W/o-emulsion formation ability. The maximum water uptake (WEM₁-value) in the w/o-emulsions was measured after 24 hours mixing.

3. W/o-emulsion stability (untreated and treated with dispersant). In these experiments, w/o-emulsions were made by mixing over periods of 1 and 24 hours. The relative water-to-oil ratio ($R_{2/1} = R_2/R_1$), was used as a measure of the w/o-emulsion stability (over the 24 hours settling period). When the w/o-emulsion breaking effectiveness of Finasol OSR-5 was tested, 70µl of dispersant (DOR = 1/50) was added to the in situ w/o-emulsion immediately after mixing. To mix the chemicals into the w/o-emulsion, the flasks were rotated for 2 minutes after the treatment before settling. The R_{2/1}-value (with R₁ from the untreated w/o-emulsion) was used as a measure for the stability of the treated w/o-emulsion.

4. W/o-emulsion inhibition effectiveness of dispersant. In these experiments, Finasol OSR-5 was premixed with the oil (before mixing with seawater) at the following 6 dispersant-to-oil-ratios (DOR): 1/500 (2000 ppm),

1/1000 (1000 ppm), 1/2000 (500 ppm), 1/10000 (100 ppm) and 0/1 (0 ppm). The $R_{2/1}$ -value (with R_1 from the untreated w/o-emulsion) was used as a measure for the w/o-emulsion inhibition effectiveness of the dispersant concentrate.

RESULTS AND DISCUSSION

Physico-chemical properties of the oils used

Crude oil is a complex mixture of hydrocarbons and non-hydrocarbons which commonly are classified into the following groups: saturates (e.g. alkanes and naphthenes), aromatics, resins (NSO-compounds) and asphaltenes (e.g. Mackay, 1987). Small differences in composition between different crudes can greatly affect the physical properties and hence the formation and stability of w/o-emulsions when oil is spilled on water. Furthermore, the composition of the crude is changed by weathering at sea.

The changes in chemical and physical properties with increased evaporative loss (topping) and photolysis are summarized in table 1.

Gullfaks crude is a naphthenic North Sea crude. The high degree of biodegradation has resulted in a low content of n-alkanes and a low wax content which gives very low pour points. The low paraffin content may also explain the relatively high density of Gullfaks crude compared to the more common paraffinic North sea crudes. The resin and asphaltene content of the Gullfaks crude is at the same low level as in most of the North Sea crudes.

Statfjord crude is a typical paraffinic North Sea crude with low density, low resin and low asphaltene content. Statfjord has a relatively high wax content which may explain the high pour point values (see table 1).

Arabian Heavy (Safaniya) crude is imported to Norwegian refineries, and is characterized by high density, high viscosity and high content of heavy end components (resins and asphaltenes). This crude is completely different to the crudes produced from the North Sea.

Photolysis. The photolysis has a significant effect on some of the physico-chemical parameters of the oils: The photolysed (20 hours) fractions have a significantly higher resin and asphaltene content compared to the corresponding 250°C+ topped fractions (see table 1). Table 1 shows that aromatics (but probably also naphthenes in the Gullfaks crude) have been photo-oxidized to more polar components (resins). The photolysis may also lead to photo-polymerization (Daling, 1984), which may explain the observed increase in asphaltene content (table 1).

Among the physical parameters, interfacial tension is particularly affected by photolysis. There is a drastic reduction in the interfacial tension for both the 1.5 and 20 hours photolysed fractions (see table 1) which clearly demonstrates the formation of surface active components by photolysis.

The photolysed (20 hours) fractions show a slightly higher viscosity compared to the corresponding 250°C+ topped fractions (particularly the Arabian Heavy crude). One reason for this may be that photo-polymerization has occurred. Other physical properties like pour point and density do not seem to be significantly influenced by photolysis.

Table 1:
Physico-chemical properties of fresh and weathered crude oils used in the experiments.

Oil type	Saturates ¹⁾ (wt.%)	Aromatics ¹⁾ (wt.%)	Resins ¹⁾ (wt.%)	Asphaltenes ²⁾ (wt.%)		Waxes ³⁾ (wt.%)	Spec. grav. (g/ml)	Pour point (°C)	Interf. tension (mN/m)	Viscosity ⁴⁾ (cP 13°C)
				"hard"	"soft"					
GULLFAKS										
Fresh	-	-	-	0.02	0.49	1.60	0.882	<-34	13	20
150°C+	-	-	-	0.02	0.52	1.72	0.893	-26	13	33
200°C+	-	-	-	0.03	0.58	1.90	0.905	-15	15	72
250°C+	52.1	40.0	6.8	0.03	0.65	2.14	0.914	-9	17	241
1.5h ph.ox	-	-	-	-	-	-	0.906	-	2.7	87
20h ph.ox	45.3	37.8	15.3	0.24	1.11	-	0.916	-	1.1	282
STATFJORD										
Fresh	-	-	-	0.01	0.39	4.14	0.834	-15	23	7
150°C	-	-	-	0.01	0.47	4.78	0.867	7	16	20
200°C+	-	-	-	0.02	0.54	5.77	0.882	11	15	57
250°C+	56.2	34.8	7.8	0.02	0.63	6.68	0.895	16	16	221
1.5h ph.ox	-	-	-	-	-	-	0.883	-	5.4	77
20h ph.ox	59.5	25.6	13.7	0.29	1.14	-	0.896	17	1.1	314
ARABIAN HEAVY										
Fresh	-	-	-	4.33	7.38	4.62	0.887	-28	20	41
150°C+	-	-	-	4.89	8.34	5.22	0.920	-23	14	241
200°C+	-	-	-	5.31	9.05	5.67	0.935	-18	18	700
250°C+	23.2	49.0	18.4	5.80	9.89	6.19	0.951	-5	17	2344
1.5h ph.ox	-	-	-	-	-	-	0.835	-	4.9	725
20h ph.ox	23.6	41.4	23.6	7.21	10.42	-	0.954	-	1.1	4350

1) Quantification by Iatroscan TLC/FID

2) Asphaltene content is calculated from data of the 250°C+ fraction, "hard" asphaltenes: IP-143 method, "soft" asphaltenes: n-pentan insoluble.

3) Wax content is calculated from data of the malthe fraction of 250°C+ (after the "hard" asphaltene separation)

4) Measured at a shear rate = 10s^{-1} .

Rates of w/o-emulsion formation (water uptake kinetics)

Due to lack of data describing the emulsification processes, the existing models for the rate of water uptake are presently very simplified and rather empirical in nature (e.g. Ross, 1986; Mackay et al., 1980). Further studies are therefore needed to obtain experimental data to validate or improve the mathematical w/o-emulsion formation models. Practical forecasting of the rate of w/o-emulsion formation for different oil qualities under a variety of conditions is important e.g. for estimating the "time-window" for a successful chemical dispersant treatment during an oil spill combat operation.

In this study, water uptake was followed over a 24 hours mixing period (see experimental). To give a more convenient description of the water uptake kinetics, the experimental data obtained were fitted to an exponential equation by Mackay et al. (1980). The theoretical exponential curve, which is best fitted to the experimental data (figure 3) was calculated.

The mixing time needed to obtain half of the maximum water content in the w/o-emulsion ($T_{1/2}$ -value) has been used as a parameter for the "relative" rates of water uptake for the different oil qualities. The calculated $T_{1/2}$ -values for the different oil fractions are plotted in figure 2. Figure 3 shows the experimental curves of the three crudes (for 200°C+ topped fractions) at 13°C.

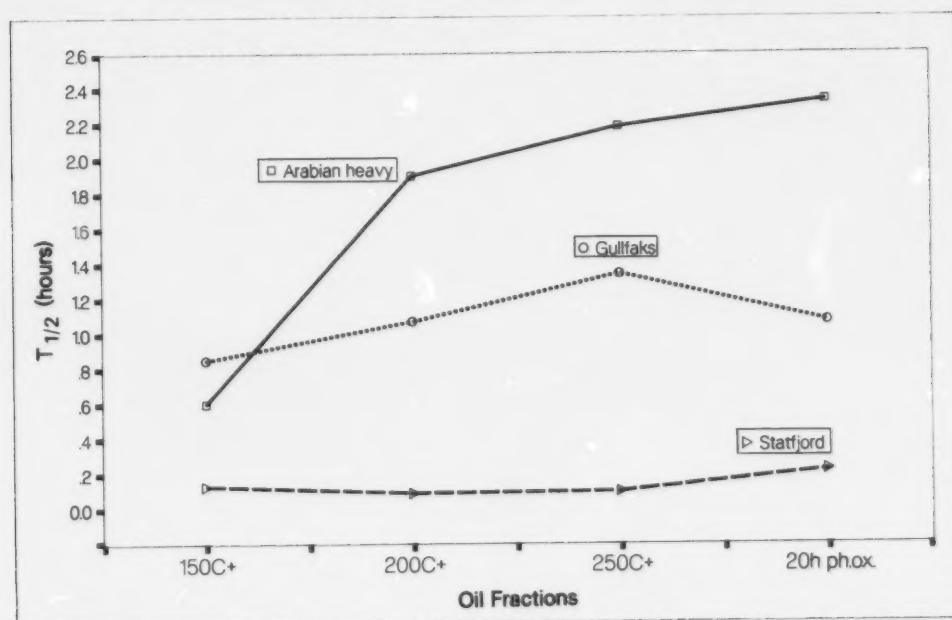


Figure 2. $T_{1/2}$ -values for the water uptake rate of the different fractions for Gullfaks, Statfjord and Arabian heavy.

The fractions from the paraffinic and wax-rich Statfjord crude have a significantly higher water uptake rate than the two other crudes (figure 2 and 3). The wax-stabilized w/o-emulsions formed by the Statfjord fractions encourage an extremely rapid water uptake. For the topped Statfjord fractions, the maximum water uptake is reached within 1 hour ($T_{1/2}$ = approx. 0.2 hour), while the Gullfaks and Arabian heavy fractions typically reach maximum water content within 8-10 hours ($T_{1/2}$ = 0.8-2.5 hours). The uptake rate for the wax-rich Statfjord crude is so fast that it is not possible to see any significant changes in uptake rate caused by variations in chemical composition due to evaporative loss. The $T_{1/2}$ -values for Gullfaks and Arabian heavy crudes in figure 2 show a slightly reduced rate of water uptake with increased evaporative loss (topping). This is probably due to increased oil viscosity which may retard the w/o-emulsion formation (Mackay, 1987).

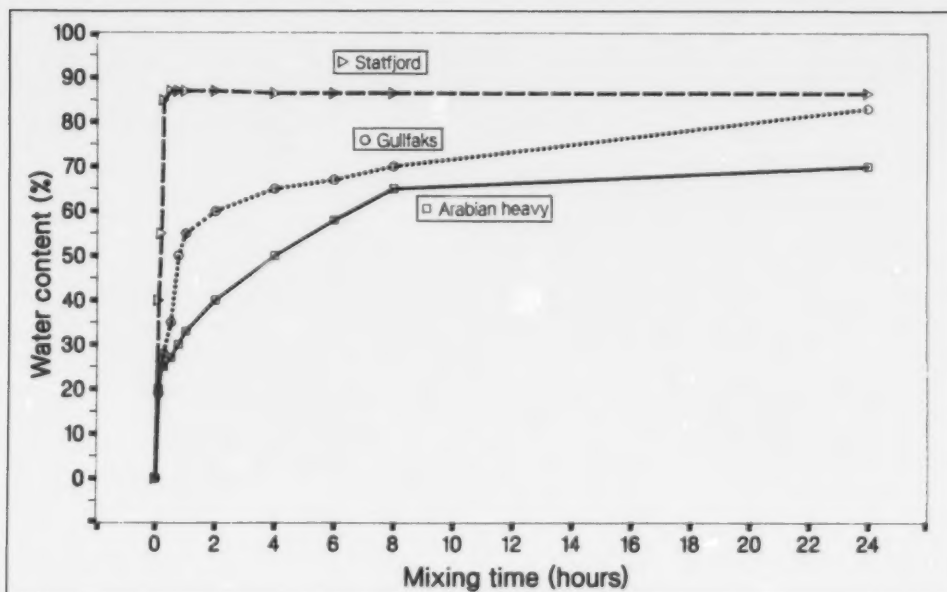


Figure 3. Rates of w/o-emulsion formation (water uptake) for the 200°C+ fractions for Gullfaks, Statfjord and Arabian Heavy.

The photolysed fraction of the Gullfaks crude has a slightly higher rate of water uptake than the corresponding 250°C+ topped fractions. This is in accordance with Mackay (1987), which suggests that a lower interfacial tension due to photolysis will enhance the w/o-emulsion formation rate. This enhanced rate in water uptake was, however, not observed in the photolysed fractions of the Statfjord and Arabian Heavy crudes (figure 2). However, this limited number of crudes make it difficult to determine if these changes in water uptake are representative. A larger number of crudes will be tested in the next part of the DIWO-project to study this question.

W/o-emulsion formation ability (maximum water uptake)

The water uptake was measured after mixing the oil fractions with sea water (see experimental) for both 1 and 24 hours. Since not all the oil fractions have reached maximum water content after 1 hour, the %EM₁-value (volume percent of water in w/o-emulsion immediately after mixing) of the 24 hours mixed w/o-emulsions was used to define maximum water uptake ability. 1 week of prolonged mixing of the Gullfaks crude indicates that no significant water uptake occurs after 24 hours mixing. The %EM₁-values obtained after 24 hours mixing of the fractions from the three crude oils are plotted in figure 4.

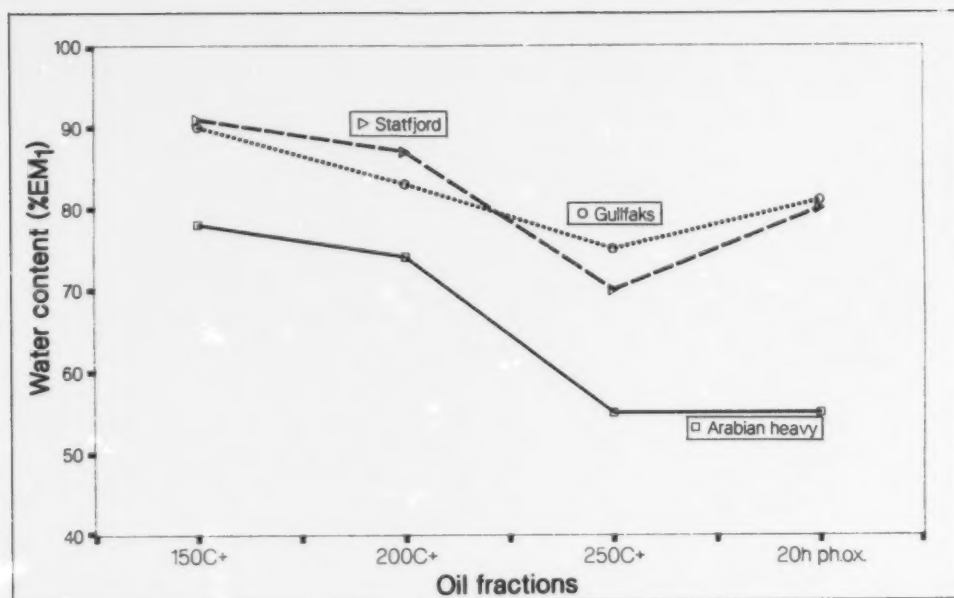


Figure 4. Maximum water uptake (%EM₁-values) for different fractions from Gullfaks, Statfjord and Arabian heavy.

Figure 4 indicates that the ability of an oil to take up water decreases with increased evaporative loss. The photolysis seems to have only a small positive effect on the maximum water uptake: the photolysed (20 hours) oils from Gullfaks and Statfjord have a slightly higher maximum water uptake than the corresponding 250°C+ topped fractions.

Viscosity of the parent oil was the physico-chemical parameter which had the highest correlation coefficient with the EM₁-values. In figure 5 the maximum water uptake is plotted against the viscosity of the parent (water free) oil. The square correlation coefficient is 0.93.

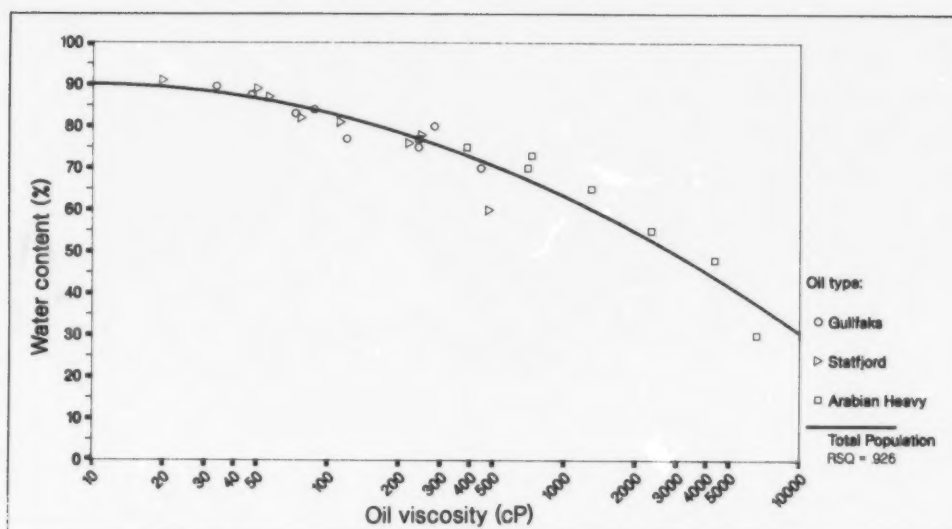


Figure 5. Maximum water uptake (EM_1 -values) plotted against the viscosity of the parent (water free) oil.

The w/o-emulsions from Gullfaks and Statfjord seems to have a similar maximum water uptake (70-91%), while the corresponding Arabian heavy oil fractions have a significantly low ability to take up water (i.e. only 30-70%). Again, this is probably due to the relatively higher viscosity of the parent oil fractions of the Arabian heavy crude (figure 5).

Stability of w/o-emulsion (untreated and treated with dispersant)

W/o-emulsions were made by mixing oil and water for 1 hour and 24 hours. The $R_{2/1}$ -value (see parameter definition) was used as a measure for the w/o-emulsion stability. The $R_{2/1}$ -value was also used as a measure for the stability of w/o-emulsions treated with finasol OSR-5 (see experimental part). The stability ($R_{2/1}$) of the w/o-emulsions (1 and 24 hour mixing, untreated and treated with OSR-5) are represented in figure 6 a-d.

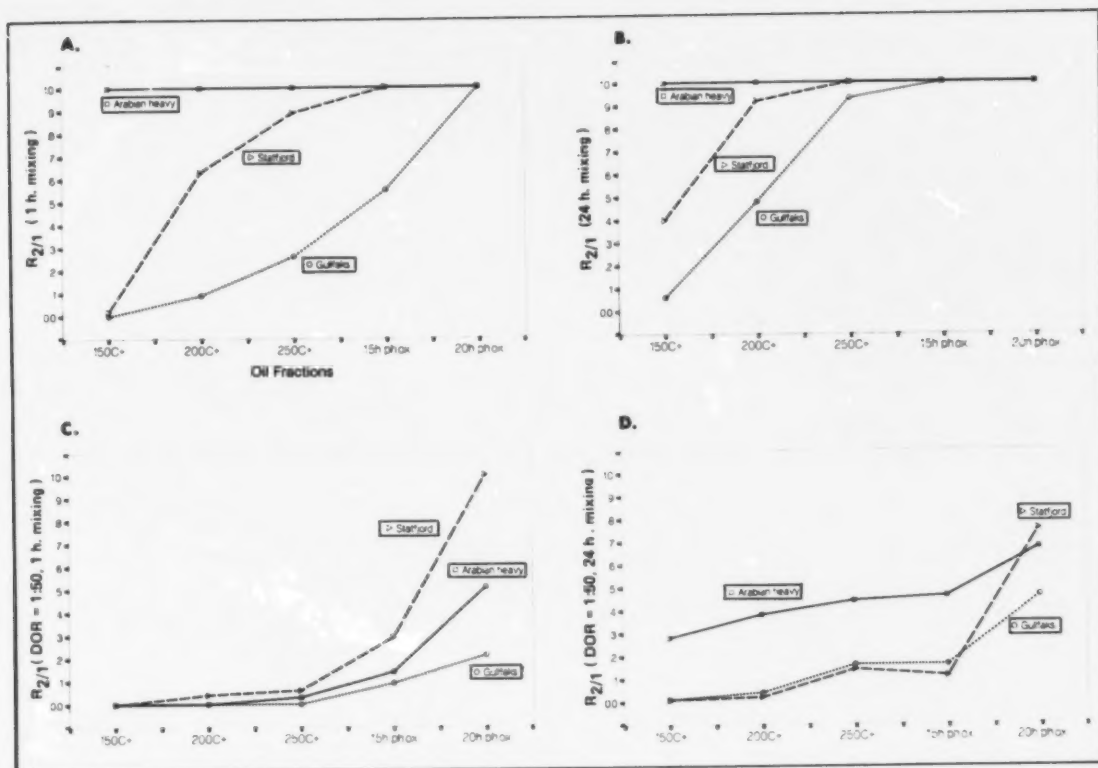


Figure 6. Relative w/o-emulsion stability ($R_{2/1}$) for:
A: 1 hour mixed w/o-emulsion (untreated).
B: 24 hours mixed w/o-emulsion (untreated).
C: 1 hour mixed w/o-emulsion treated with Finasol OSR-5 (DOR=1:50).
D: 24 hours mixed w/o-emulsion treated with Finasol OSR-5 (DOR=1:50).

Mixing time had a great influence on the stability of the w/o-emulsions. Only the most weathered fractions of the Gullfaks and Statfjord crudes formed stable w/o-emulsions after a mixing time of 1 hour (figure 6a), while figure 6b shows that for the w/o-emulsions mixed for 24 hours, only the lightest fractions of Gullfaks and Statfjord crudes formed unstable w/o-emulsions which coalescence during the 24 hours settling time.

The influence of mixing time on the stability of the w/o-emulsions may reflect the relatively larger amount of smaller water droplets in the w/o-emulsions mixed over 24 hours (see figure 7a-b). This agrees with the me-

chanisms of formation and stability of w/o-emulsion postulated by Mackay (1987). The larger fraction of smaller water droplets (typically 10-50 μm) produced after 24 hour mixing will have a lower separation speed in the continuous oil phase than larger water droplets (typically 60-120 μm) produced after 1 hour mixing.

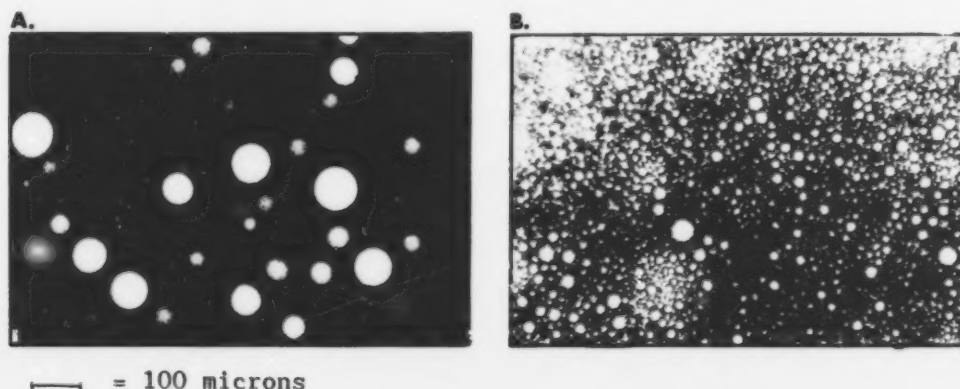


Figure 7. The influence of mixing time on the water droplet size in the w/o-emulsion (Arabian Heavy 150°C+).
A: 1 hour mixing, B: 24 hour mixing

The asphaltene/resin rich Arabian Heavy w/o-emulsions show extremely high stability. Irrespective of weathering degree and mixing time, none of the w/o-emulsions from this crude showed any breaking tendency during a settling time of 24 hours (figures 6 a and b). Even centrifugation of the w/o-emulsions did not settle the water droplets in the w/o-emulsions (2500 rpm for 10 min at 20°C). This high stability may be related to the high asphaltene content in Arabian Heavy crude (4.33 wt%, IP-method 143).

Compared to Arabian Heavy, the Statfjord crude shows a lower w/o-emulsion stability. However, the Statfjord w/o-emulsions were significantly more stable than the Gullfaks w/o-emulsions (figures 6 a and b). This may be connected to the higher wax content of the Statfjord crude (4.14 wt.%) compared to the Gullfaks crude (1.60 wt.%). The asphaltene content in both the Gullfaks and Statfjord crudes is very low (< 0.05 wt% IP 143).

Increased stability is observed with increased topping (for Gullfaks and Statfjord crudes). This may partly be explained by the increase of naturally occurring film-forming components due to increased evaporative loss (see table 1). Furthermore, increased viscosity of the w/o-emulsion lowers the settling rate of the water droplets in it (Ross, 1986).

Figure 6 a and b shows that the photolysis also has a marked influence on the stability of the w/o-emulsion. Even the fraction photolysed for 1.5 hours is significantly more stable than the corresponding non-photolysed 200°C fraction. It is therefore evident that surface-active components

which are produced (cf. the increased contents of asphaltenes and resins in table 1) during the illumination process act as w/o-emulsion stabilizing agents. Furthermore, photomicrographs indicate that slightly smaller water droplets are formed in the photolysed w/o-emulsions (figure 8). This also increase the w/o-emulsion stability (Ross, 1986).

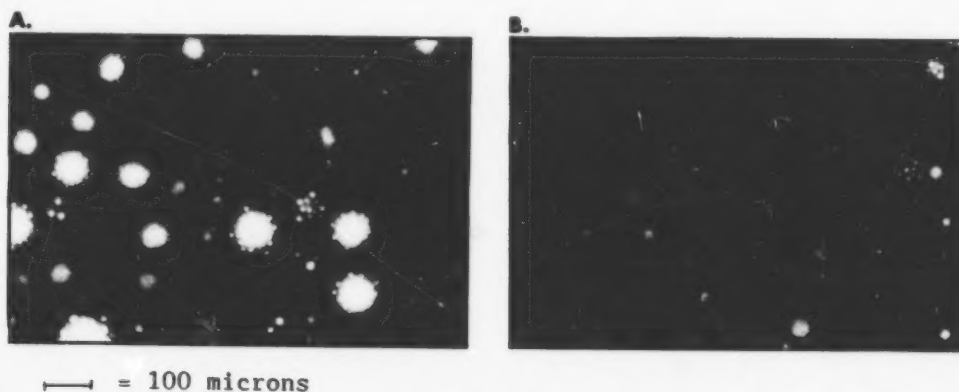


Figure 8. The influence of photolysis of oil on the droplet size of the water in the w/o-emulsion.
A: Gullfaks 250°C+, **B:** Gullfaks photolysed for 20 hours.

Treatment of the w/o-emulsion by Finasol OSR-5 produced a significant reduction in the water content (breaking of the w/o-emulsion). The relative effectiveness of Finasol OSR-5 (see figures 6 c-d) appears to be closely related to the stability of the w/o-emulsions.

Figure 6 c-d shows that it is more difficult for OSR-5 to break the 24 hour w/o-emulsions than the 1 hour w/o-emulsions. This again may be related to the relatively higher stability (smaller water droplets) of the 24 hour w/o-emulsions (figure 7). Within the same crude, the 150°C+ fraction showed the greatest reduction in water content after treatment by OSR-5. Furthermore, the dispersant was much less effective on the w/o-emulsions of the fractions photolysed for 20 hours than on the corresponding 250°C+ topped (non-photolysed) fractions.

W/o-emulsion inhibition effectiveness of Finasol OSR-5 (premixing at different DORS)

These experiments illustrate the ability of a dispersant concentrate (Finasol OSR-5) to inhibit w/o-emulsion formation of an oil. The dispersant was added (premixed) with the oil at very low concentrations (100-2000 ppm, see experimental part). W/o-emulsion formation tendency and stability was tested with these "spiked" oils as described previously (24 hours mixing time followed by a 24 hour settling time). The $R_{2/1}$ -values calculated with the R_1 -value from the untreated w/o-emulsions, were used as a measure for the w/o-emulsion inhibition effectiveness of Finasol OSR-5.

Figure 9a-c shows the w/o-emulsion inhibition effectiveness of Finasol OSR-5 ($R_{2/1}$) at different dispersant-to-oil ratios for the three crudes.

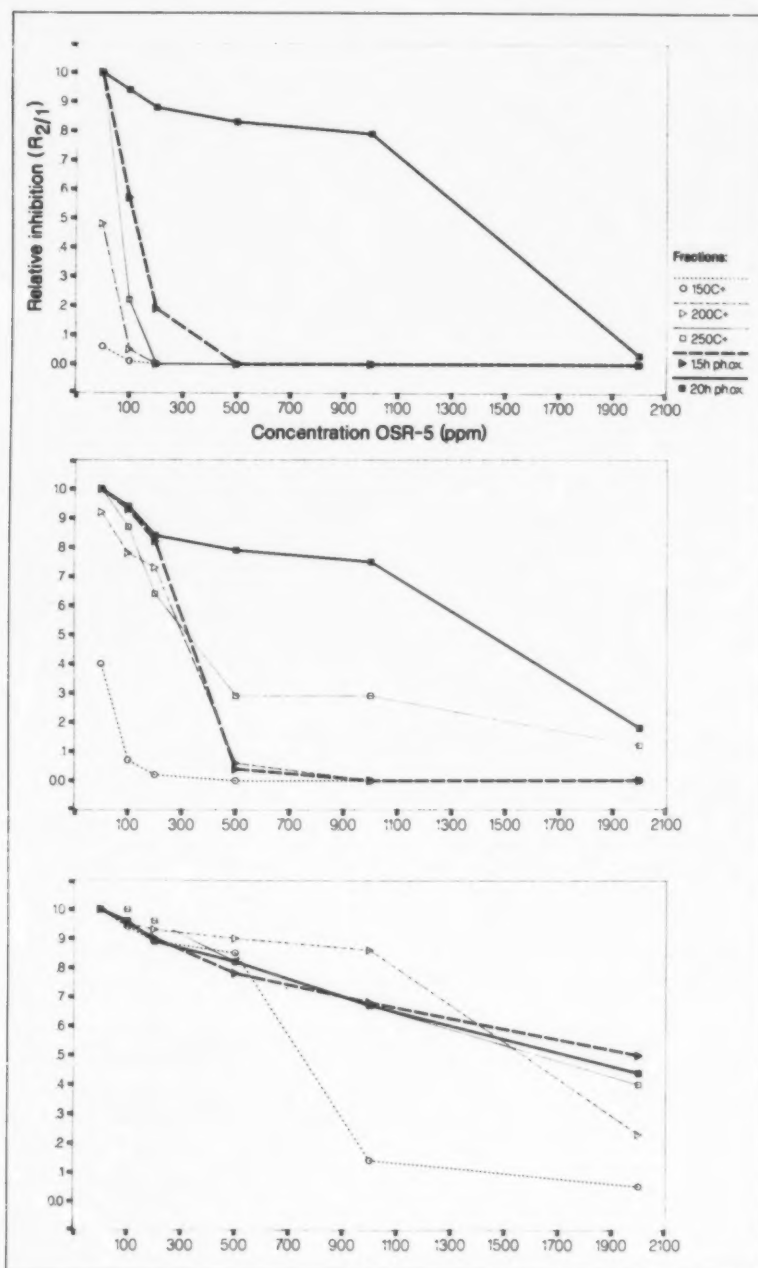


Figure 9. The effectiveness of Finasol OSR-5 to inhibit the w/o-emulsion formation.

The reduced uptake of water relative to the corresponding untreated oil reflects the dosage of chemical premixed into the oil (e.g. figure 9a). To obtain the same reduction ($R_{2/1}$ -value) on increasingly topped fractions, there is a need for an increased DOR. The 250°C+ fraction, for example, needs a larger DOR compared to e.g. the 200°C+. The inhibition effectiveness of the premixed dispersant was significantly lower on the fractions photolysed for 20 hours (on Gullfaks and Statfjord) than on the corresponding 250°C+ topped fractions. This again indicates that components produced during photolysis (asphaltenes/resins) interact with the emulsion inhibition performance of the dispersant.

Figure 10 illustrates the variation in the amount of dispersant needed to inhibit water uptake in the different crudes. Photolysis has a tremendous influence on the amount of dispersant needed for the Gullfaks and Statfjord crudes. Premixing of OSR-5 into the photolysed fractions of Arabian Heavy produced no significant differences relative to the corresponding 250°C+ topped fraction. The reason for this may be that the amount of photolysed components produced is probably low relative to the high content of indigenous surface-active components in this particular crude (table 1).

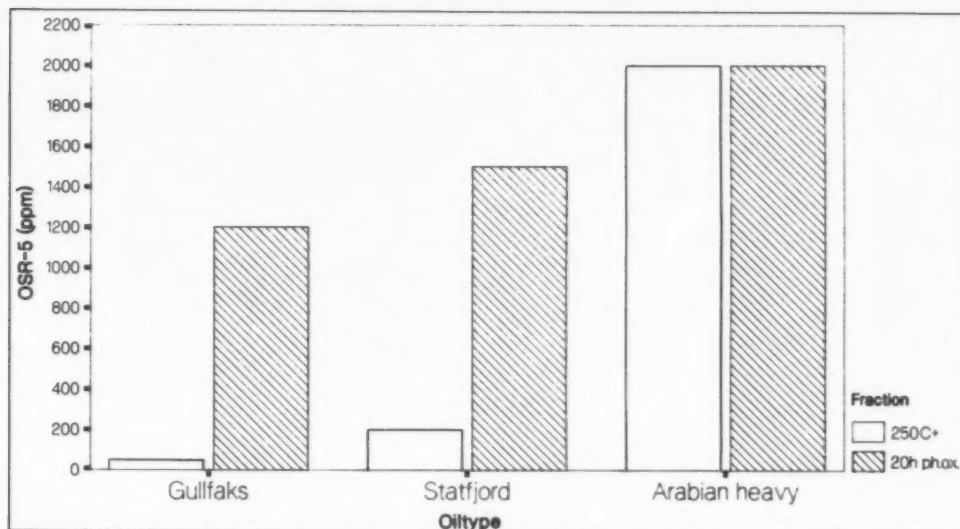


Figure 10. The amount of Finasol OSR-5 needed to inhibit the formation of w/o-emulsion with 60 percent (relative to untreated oil fractions).

SUMMARY AND CONCLUSIONS

This paper presents a laboratory study on the w/o-emulsion formation tendency and w/o-emulsion stability properties of three crude oils which are produced and/or transported in Norwegian coastal waters.

The aim of the study has been to obtain information concerning the following:

- * the rate of w/o-emulsion formation
- * the maximum water content in w/o-emulsion
- * the stability of w/o-emulsions (untreated and treated with a dispersant concentrate)
- * the w/o-emulsion inhibition effectiveness of a dispersant concentrate

These parameters have been investigated in relation to a gradually increased degree of weathering for each crude (including evaporative loss and photolysis). It is concluded that the characteristics of the w/o-emulsions are highly dependent on the physico-chemical composition of the crude. Furthermore, the alteration of the physico-chemical composition due to weathering of the crude may have significant effect on the w/o-emulsion properties:

Water uptake rate

The rate of water uptake is very different in the three crudes. The wax-rich Statfjord fractions have significantly higher rates of water uptake than the naphthenic Gullfaks and asphaltene/resin-rich Arabian Heavy crudes. Photolysis of the oils appears to have only minor effect.

Maximum water uptake

The maximum water uptake ability of the w/o-emulsions depends largely on the viscosity of the parent oil; low viscosity oils give w/o-emulsions with high water contents, while more viscous oils give w/o-emulsions with lower water contents.

Emulsion stability

The stability of the w/o-emulsions formed depends particularly on the chemical composition of the crudes used. Waxes, resins and asphaltenes all appear to act as w/o-emulsion stabilizing agents. Photolysis of the oils has a tremendous effect on the w/o-emulsion stability (photolysis giving a higher resin and asphaltene content).

Finasol OSR-5 is typically 2-6 times more effective in breaking w/o-emulsions formed by topped Gullfaks and Statfjord crude oil fractions, than w/o-emulsions formed by Arabian heavy crude oil fractions.

Finasol OSR-5 appears to "displace" the w/o-emulsion stabilising components at the w/o-interface. The effectiveness of OSR-5 to break w/o-emulsions depends largely on the stability of the w/o-emulsions formed. The correlation coefficient between the relative w/o-emulsion stability and the relative w/o-emulsion breaking effectiveness of OSR-5 is 0.73 (with a significance of 2 percent).

Emulsion inhibition

Premixing of small amounts of Finasol OSR-5 into oils before mixing with sea water indicated that Finasol OSR-5 has great potential to inhibit/reduce the formation of w/o-emulsions. However, the concentrations (DOR) needed to obtain this depend largely on the type of crude and the degree of weathering (evaporation and photolysis) of the particular oil.

From a practical point of view, these tests demonstrate the desirability of treating a slick with a low dosage of dispersant (100-2000 ppm, depending on crude and degree of weathering) as soon as possible after discharge of the

oil to retard and reduce the water uptake ability. Thereafter, it can be possible to treat the slick again several hours later with higher dosages which are more common for dispersant application (DOR = 1:50 - 1:25).

ACKNOWLEDGEMENTS

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RESULTS OF BEACH STUDIES AND CHEMICAL ANALYSES FROM THE BIOS EXPERIMENTAL SITE AND FROM THE "METULA" SPILL SITE

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INTRODUCTION

A sequence of studies that began in 1981 has focused on the fate of stranded oil on cold-climate shorelines. In 1987, two projects were carried out as part of this long-term program:

- (1) the site of the 1981 BIOS experimental spill was revisited and resampled, and
- (2) site visits were made to the area of the 1974 spill from the VLCC "METULA" in the Strait of Magellan, Chile.

Field reports on these two projects (Owens and Robson, 1987; Owens and Humphrey, 1988) provide site descriptions, details on field and laboratory methods, and complete sets of the results.

The purpose of this paper is to review the results in the context of previous projects and to compare data from the two 1987 projects.

BIOS 1987 RESULTS

Control Plots

Sediment samples were collected from two backshore (non-marine) control plots, designated T1 (aged crude oil) and T2 (emulsion), that were established in 1980. There has been little change in the oil content through time, with the exception of an initial decrease in the reduction of the oil content of the T1 surface sediments as light fractions of the crude oil were weathered. The oil at this site has never formed a hard surface crust nor has it resembled an asphalt pavement and it can be assumed that one of the elements necessary for the formation of an asphalt pavement is contact with (sea) water.

Mean total hydrocarbon values of $27,000 \text{ mg kg}^{-1}$ for T1 and $26,250 \text{ mg kg}^{-1}$ for T2 are higher than 1983 and 1985 values, but are similar to 1981 and 1982 results. The trends that were apparent in the 1983 and 1985 data are now thought to have been affected by the sampling pattern and that in reality there has been little or no change in the surface or subsurface oil content of the sediments after the 1980 data set.

Bay 11 - Experimental Spill Site

In 1981, 15 m^3 of aged crude oil were released onto the nearshore waters of a small bay and allowed to strand on the adjacent, sheltered gravel beach (Sergy and Blackall, 1987). Previous field projects had been conducted in 1982, 1983, 1985 and 1986 to measure the distribution of the surface oil cover and to collect sediment samples for total hydrocarbon and GC/FID analyses.

Bay 11 - Oil Cover

The measured surface oil cover of 2240 m^2 in 1987 is half that of the 1985 cover (4440 m^2) (Table 1). The length of oiled beach in 1987 was only slightly reduced from 1985 (180 to 160 m) as the major changes in oil distribution occurred in the lower intertidal zone rather than in the continuous, but narrow, layer of oil at the mean high-water level (Figure 1). Visual comparison of the 1985 and 1987 oil distribution maps (Figure 1) indi-

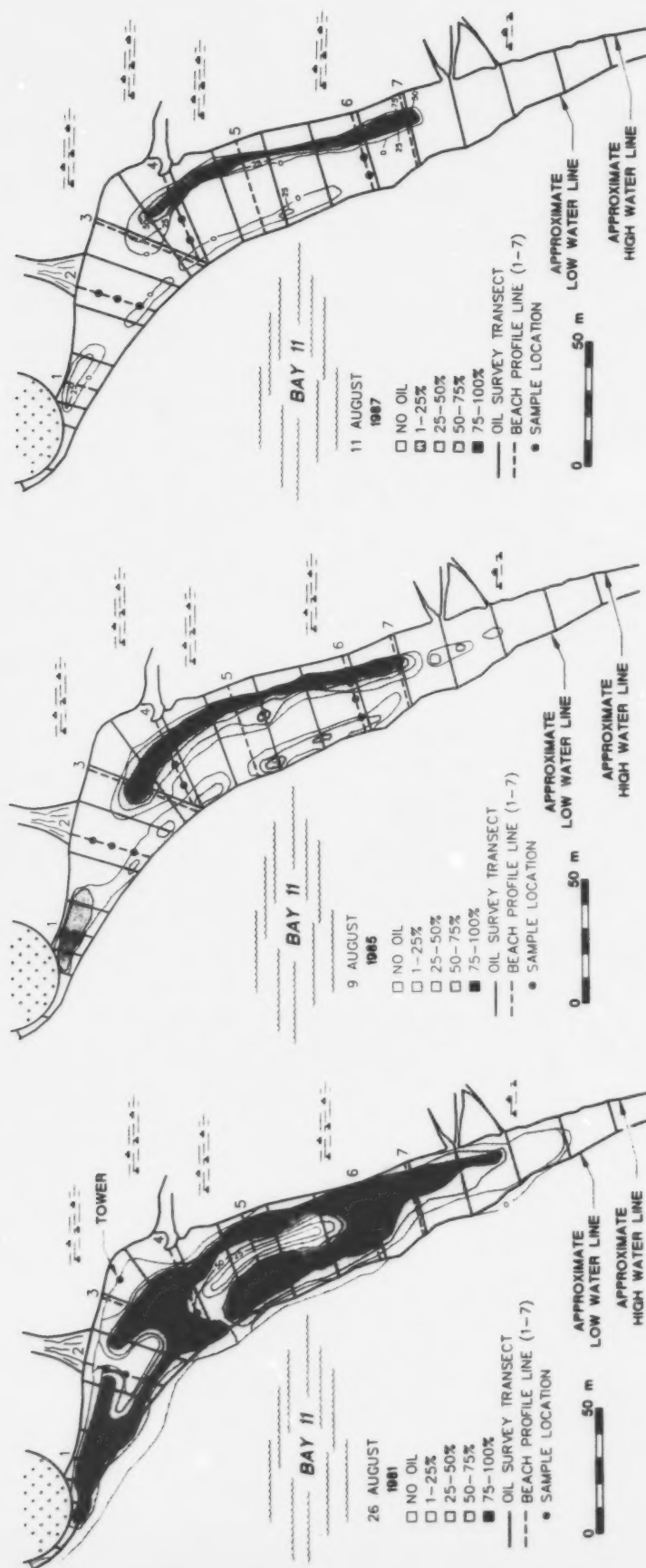


Figure 1 Bay 11 Surface Oil Cover Maps: 1981, 1985 and 1987

TABLE 1 — BAY 11—SURFACE OIL DISTRIBUTION: 1981-1987

YEAR	SURFACE OIL COVER BY CATEGORY (m ²)					TOTAL OILED AREA (m ²)	LENGTH OF OILED BEACH (m)
	0%	0.1-24%	25-49%	50-74%	75-100%		
1981	6200	2015	1700	1145	3710	8570	275
1982	5170	5200	1775	1320	1305	9600	250
1983	10845	2120	840	350	615	3925	190
1985	10330	1830	1440	660	510	4440	180
1987	12530	1040	560	280	360	2240	160
% Change 1981-1987	+102	-48	-67	-76	-90	-74	-42

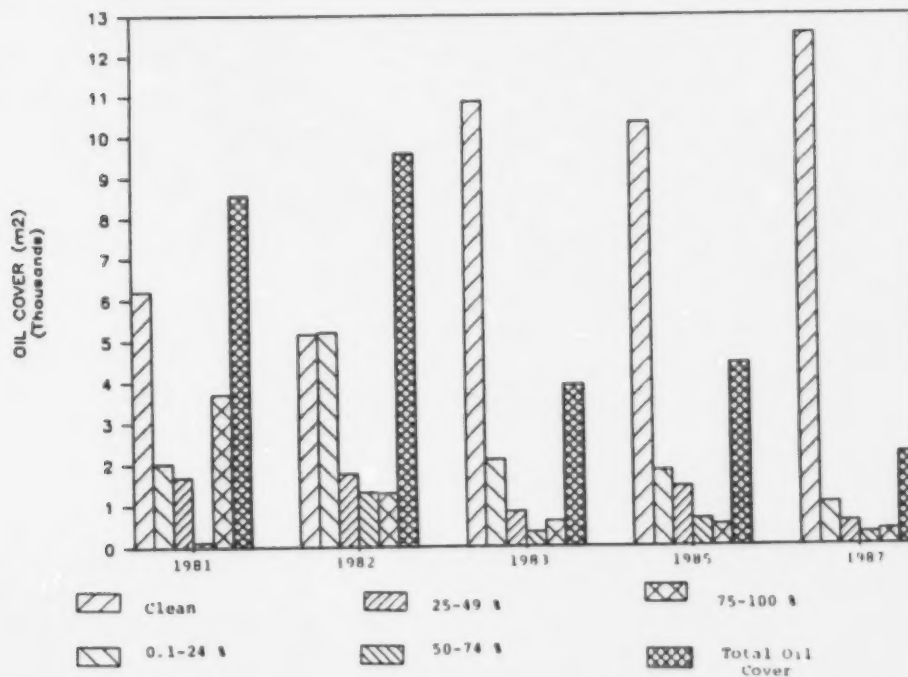


Figure 2 Changes in Bay 11 Measured Surface Oil Cover Categories: 1981-1987

cates that the basic pattern of the oil cover did not change significantly but that the actual cover was significantly reduced in all areas.

The breakdown of the oil cover by category (Table 1 and Figure 2) indicates a reduction in all of the oil categories between 1985 and 1987, with the least reduction (of 30%) occurring in the 75-100% range. In 1981, 43% of the total oiled area, almost half, had a cover of 75 to 100%, but by 1987 only 16% of the total oiled area was in this category. In 1981 24% of the oil cover was in the 0.1 to 24% category, whereas in 1987 this value had increased to 46%, so that the trend of an increasingly lighter oil cover is shown clearly. In terms of the area or surface distribution of oil, not only did the total oiled area decrease by 74% over the period 1981 to 1987, but the distribution changed from a heavy to a light oil cover. However, as will be discussed later, in terms of the volume of oil, a significant proportion of the remaining oil remains locked in the heavy oil cover category.

Bay 11 - Total Extractable Hydrocarbons

The repetitive intertidal surface sample results indicate that the highest oil concentrations remain in the upper intertidal zone, associated with the area of highest oil cover. The mean values for the repetitive upper, middle and lower intertidal samples are 16340, 1750, and 36 mg kg^{-1} , respectively. The upper intertidal zone samples show high, but variable, values from 1982 onwards (Figure 3), whereas the middle and lower intertidal zone samples show consistently low relative concentrations.

The surface samples that were collected subjectively, to illustrate oil concentrations from different segments of the intertidal zone, are consistent with previous data and show highest values from the beach face pavement (mean 16,200 mg kg^{-1}). When the repetitive results (set (a) in Table 2) are compared with the additional data set (set (b) in Table 2), the mean values are very similar (6,800 and 6,360 mg kg^{-1}) and this indicates that the two data sets are probably representative of the average oil concentrations on the oiled sections of the beach.

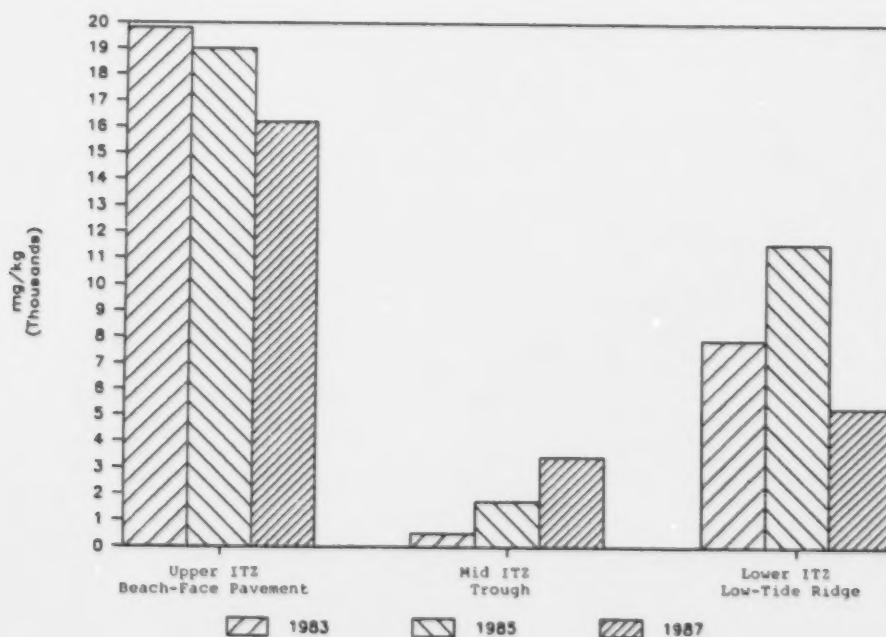


Figure 3 Bay 11 Cross-Beach Total Hydrocarbon Concentrations: 1983-1987

TABLE 2

TIME SERIES OF BAY 11 MEAN TOTAL EXTRACTABLE HYDROCARBON
CONCENTRATIONS AND COMPUTED OIL VOLUMES: 1981-1987

Date	Number of Samples	Mean Surface Total Hydrocarbon Concentration (mg kg ⁻¹)	Surface Oil Volume	
			100% Ea. Method	Volume Method
19 Aug 1981	6	17,400	5.3 m ³	5.3 m ³
20 Aug 1981	9	7,100	-	2.2
28 Aug 1981	9	6,700	-	2.0
15 Sept 1981	9	5,900	-	1.8
10 Aug 1982	9	4,400	3.6	1.5
16 Aug 1983 (a)	9	11,870	-	1.6
16 Aug 1983 (b)	10	4,800	-	0.6
16 Aug 1983 (c)	19	8,150	1.5	1.1
9 Aug 1985 (a)	9	1,980		
9 Aug 1985 (b)	14	12,530		
9 Aug 1985 (c)	23	8,400	1.3	1.3
12 Aug 1987 (a)	8	6,800		
12 Aug 1987 (b)	21	6,360		
12 Aug 1987 (c)	29	6,480	0.9	0.52

Note: In 1983, 1985 and 1987 the (a) samples were collected at the same nine locations as the previous sample sets; the (b) samples were at additional selected locations; and (c) = (a) + (b).

TABLE 3 — CHANGES IN BAY 11 SHORELINE CONTAMINATION PARAMETERS: 1981-1987

	Initial (August 1981)	+ 4 Years (August 1985)	% change from 1981	+ 6 Years (August 1987)	% change from 1981
Length of Oiled Beach	275 m	180 m	67	160 m	58
Total Oiled Area	8,570 m ²	4,400 m ²	51	2,240 m ²	26
Average Oil Cover	57%	27%	47	36%	63
Equivalent Area of 100% Cover	4,850 m ²	1,200 m ²	25	800 m ²	16
Volume of Oil on Beach	5.3 m ³	1.3 m ³	24	0.52 m ³	10
Volume of Contaminated Sediments:					
(a)	97 m ³	32 m ³	33	16 m ³	16
(b)	860 m ³	440 m ³	51	220 m ³	22

(a) Calculated using weighted surface cover values.

(b) Simple length x width x depth calculation.

Bay 11 - Oil Volumes

The computed oil volume, based on the total oiled area and the average t-h (total-hydrocarbon content) concentration (Owens et al., 1987), gives a value of 0.52 m³ for the 1987 data set (Table 2). This value compares to an initial (1981) volume of 5.3 m³ and a 1985 volume of 1.3 m³. The Equivalent Area calculation, which is based on surface oil distribution only, produces a volume of 0.9 m³ for 1987.

The volume of oil-contaminated sediments that would have had to be removed in 1987, if the beach were to have been cleaned, was on the order of 220 m³, approximately one-quarter of the original volume of oil-contaminated sediments. The actual volume of contaminated sediments had been reduced to 16 m³, or about one-sixth of the original total (Table 3).

Bay 11 - Weathering Ratios

The ratios determined in 1987 from GC analyses of the sediment samples follow the patterns set in previous years. In general, no difference in weathering may be identified although samples with a high t-h exhibit ratios that are indicative of only moderately weathered oil, whereas samples with low t-h values are more weathered.

Bay 11 - Asphalt Pavement

The pavement was still very evident in 1987 as a discrete feature of the intertidal zone and in terms of the high t-h concentrations. There was a slight increase in the total area of the pavement, compared to 1985, and in the volume of contaminated sediments (Table 4). More significant than these minor changes is the proportion of remaining oil and contaminated sediments that are contained in the pavement. This proportional increase is

TABLE 4 — BAY 11 ASPHALT PAVEMENT DATA: 1983-1987

Year	Pavement Area	Volume of Contaminated Sediments in Pavement	Percent of Total Contaminated Sediments on Beach	Volume of Oil in Pavement (Volume Method)	Percent of Total Oil Volume on Beach
1983	325 m ²	16.25 m ³	60%	0.6 m ³	55%
1985	205 m ²	10.25 m ³	32%	0.35 m ³	27%
1987	220 m ²	11.00 m ³	70%	0.32 m ³	61%

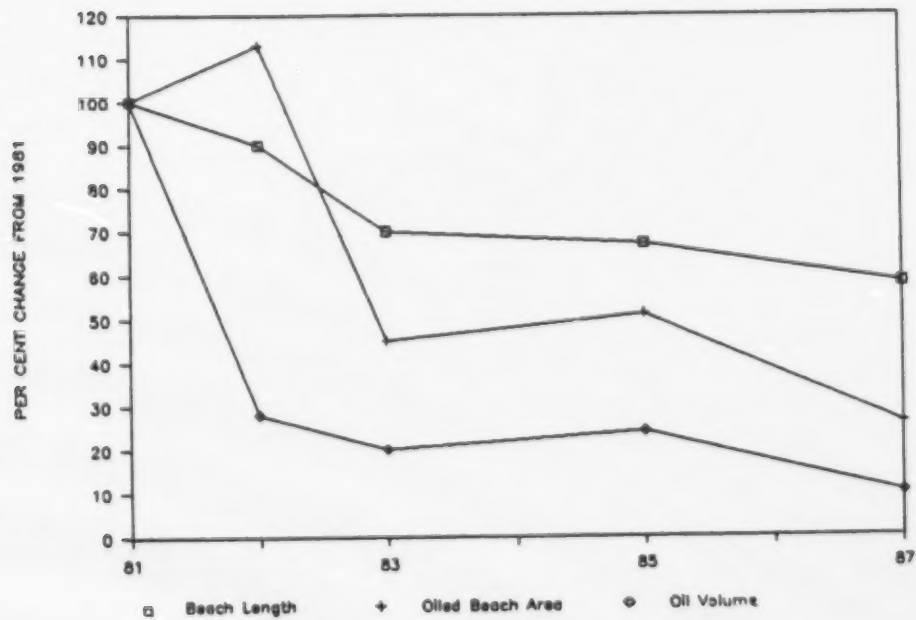


Figure 4 Changes in Stranded Oil at Bay 11 by Length, Area and Volume: 1981-1987

due to natural cleaning of the less contaminated sediments and to the lack of cleaning in the more resistant pavement area. The oil in the pavement was considerably softer and more malleable, i.e., it had a lower viscosity, than in 1983 and 1985, although the weathering indices indicate that the samples remain relatively unweathered prior to the site visit and any explanations of this low viscosity would be purely speculative.

Bay 11 - Discussion

The two most significant points to emerge from the 1987 field study are (1): the continued slow reductions in the contaminated area and volume of oil remaining on the intertidal zone (Table 3 and Figure 4), and (2): the continued presence of the asphalt pavement which contains a high proportion of the remaining oil.

Much of the intertidal area has been cleaned naturally and in 1987 85% of the beach was free of visible oil (versus 42% in 1981). Although the fine grained sediments in the mid-beach trough were visually clean (Figure 1), the t-h sample analyses indicate that they still contain oil (Figure 3). The remaining visual oil is concentrated on the beach-face pavement, with a secondary concentration on the low-tide ridge. On the latter, the oil had a dull brown, color and the distribution was very patchy; only one value greater than 25% oil cover was recorded. The pavement oil-in-sediment concentrations remain high, and the highest single value ($35,000 \text{ mg kg}^{-1}$) is the same magnitude as the highest from the backshore control plot (T1). The pavement remains as a narrow, but continuous, line of relatively unweathered oil in the upper intertidal zone.

1987 "METULA" RESULTS

As part of the program to examine stranded oils, samples were collected from the site of the 1978 "AMOCO CADIZ" spill in 1985 (Owens and Robson 1985) and from the site of the 1974 wreck of the "METULA" in 1987 (Owens and Robson 1987). The samples from the "AMOCO CADIZ" were analyzed as part of the BIOS project in 1985 (Humphrey and Hope 1986).

Analyses of "METULA" Stranded Oil

Total hydrocarbon analyses of the "METULA" samples indicate that, where present in the Strait of Magellan, the stranded oil is abundant. The highest concentration observed was almost 5% by weight, with most samples containing more than 1% hydrocarbon. Typically, the highest values are associated with sand material, whereas the lower values are associated with sand-cobble material (Table 5).

The GC/FID analyses of the samples may be divided into three types, as typified by the traces in Figure 5, and are labeled as types A, B, and C.

Type A hydrocarbon compositions (Figure 5a) are made up of natural n-alkanes and isoprenoids probably derived from the copious amounts of phytoplankton associated with the beach materials, with varying amounts of n-alkanes from n-C₂₃ to about n-C₃₃, which may be from the "METULA" oil.

Other areas were exemplified by hydrocarbon compositions made up predominantly of UCM (Type B, Figure 5b). Some samples, however, were composed of only moderately weathered oil (Type C, Figure 5c). These latter samples include clearly resolved n-alkane components in a typical petroleum related envelope with an underlying UCM.

A suite of samples from Espora Marsh Creek, all from above the spring high water line, included all three of these compositional types (Figure 6). These samples were also visually different and were located within a few meters of each other. Sample 52 was a hard, malleable pavement, 53 was soft and oily, whereas 54 was very hard and had to be chipped to collect the sample. The compositional traces differ in a consistent fashion: the soft, oily sample is Type C, only moderately weathered, including n-alkanes from

TABLE 5 — SUMMARY OF "METULA" T-H (TOTAL HYDROCARBON)
SEDIMENT SAMPLE CHARACTERISTICS AND ANALYTICAL RESULTS

SITE	BEACH LOCATION				SEDIMENTS				OIL TYPE				t-h Content (mg kg ⁻¹)
	litt	bfs	m-shw	+shw	fine	sd	sd/pb	pb/cb	latex	mousse	soft asph.	hard asph.	
25 Banco Orange				•	•						•		10000
26 Espora Creek				•	•						•		30000
27 Espora Creek								•					22000
28 Espora Spit		(•)	•									•	12000
29 Espora Spit		(•)	•									[*] [*]	9300
30 Espora Spit		•			•						•		23000
31 Espora Spit		•			•						•		18000
32 Espora Beach		•									•		13000
33 Espora Beach		•									•		280
34 Espora Beach		•										•	9200
35 Espora Beach		•										•	13000
36 Daniel Este													24000
37 Punta Malvinas				•	•			•					11000
38 Punta Malvinas				•				•				•	24000
39 Punta Malvinas				•	•						•		36000
40 Rio Oscar				•	•							•	12000
41 Rio Oscar				•				•				•	10000
42 Punta Baxa				•	•							•	50000
43 Espora Beach					•					•			53000
44 Espora Beach	•				•				•				32000
45 Espora Beach	•												14000
46 Espora Beach	•											•	9100
47 Espora Beach	•											•	9800
48 Espora Beach	•				•					•			17000
49 Espora Beach		•								•			16000
50 Espora Beach		•						•			•		47000
51 Espora Beach		•				•				•			25000
52 Espora Beach						•						•	32000
53 Espora Beach				•									48000
54 Espora Beach				•							•	[*]	7300

notes: (•) indicates that the sample was taken from the beach-face slope, but above the mean high water level;
[*] indicates that the sample had to be chiselled from the asphalt pavement.

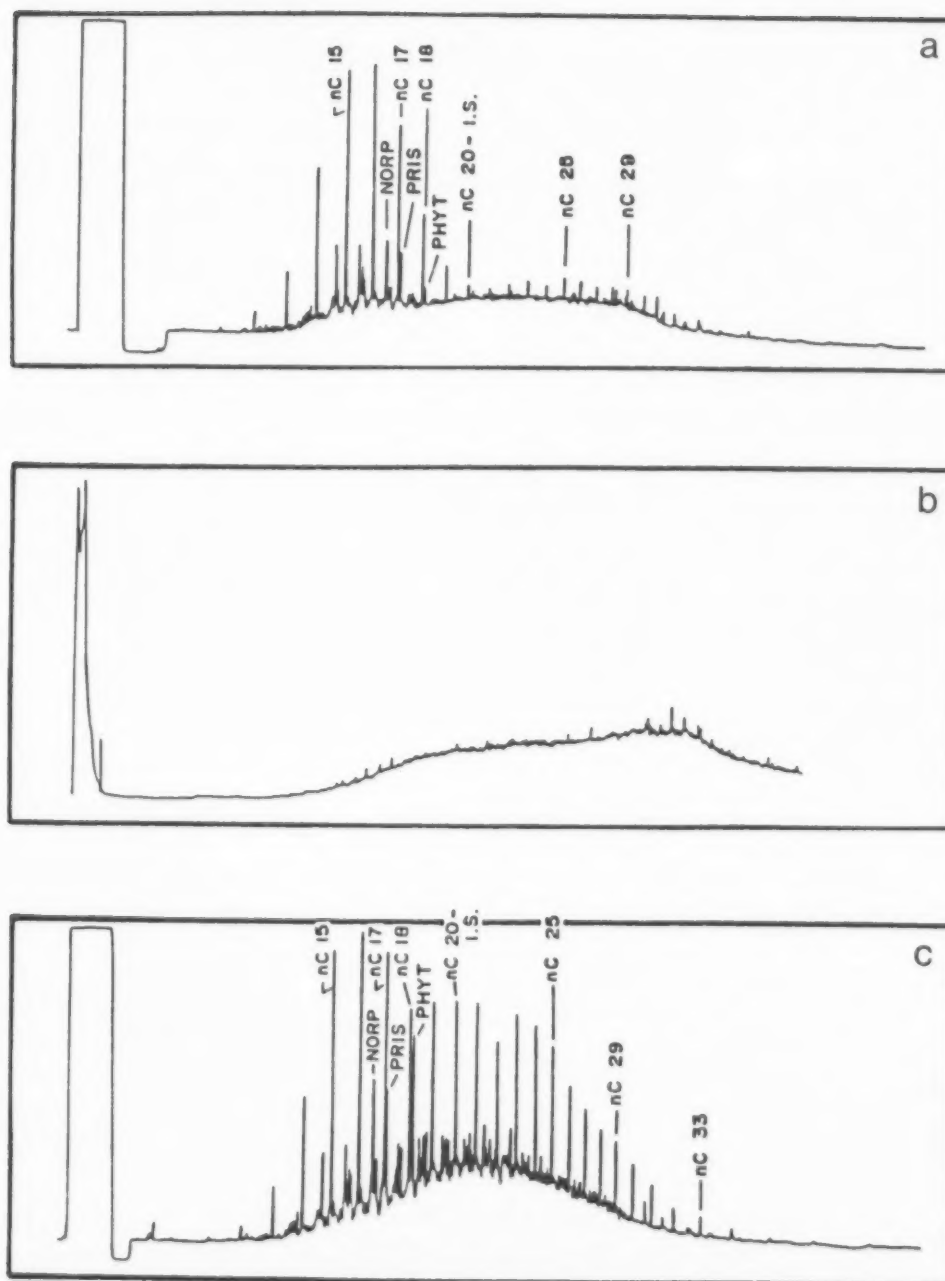


Figure 5

"Metula" GC/FID Traces:

(a) natural hydrocarbons

(b) weathered oil

(c) moderately weathered oil

(sample 7)

(sample 8)

(sample 11)

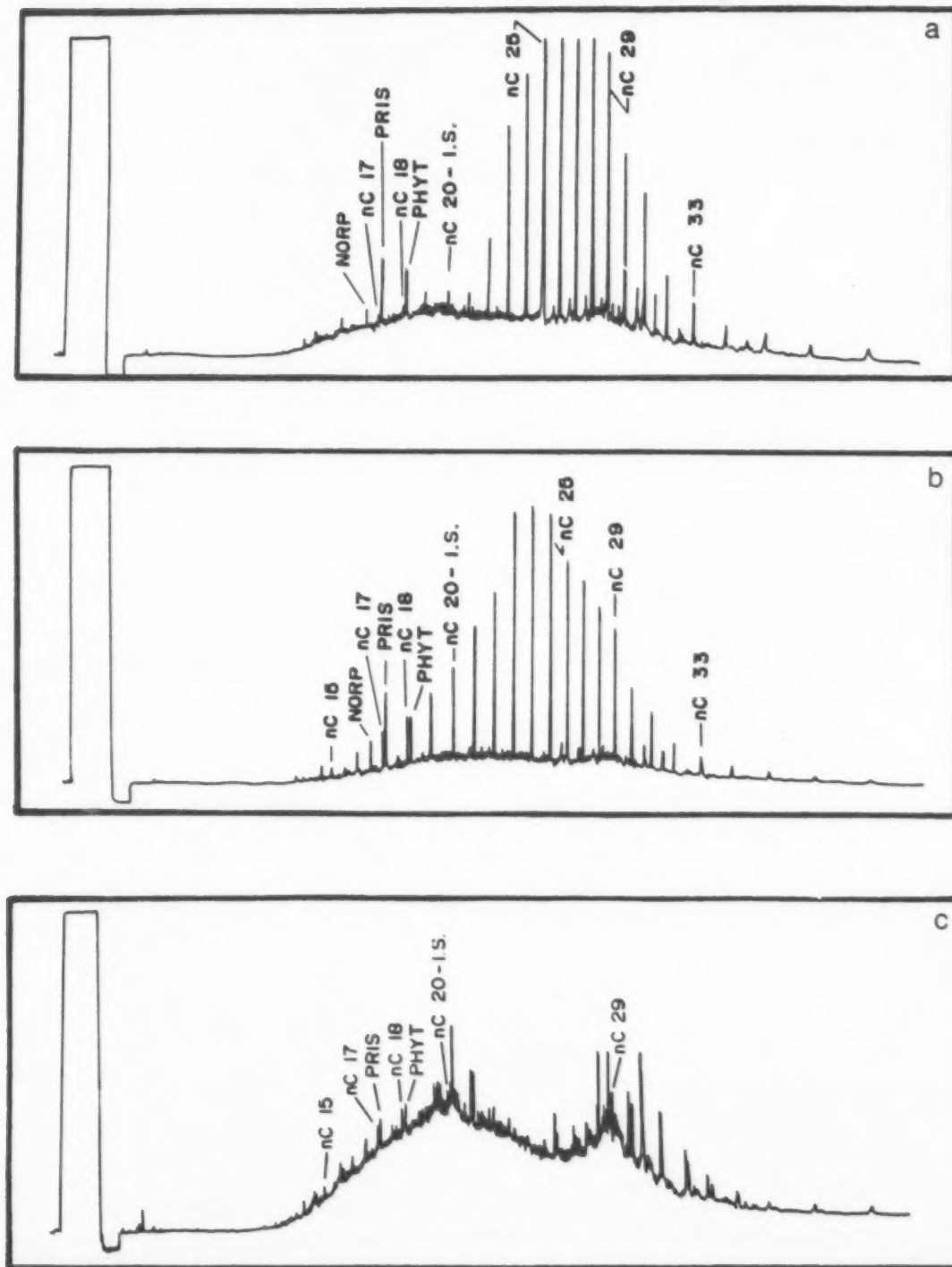


Figure 6

"Metula" GC/FID Traces:

- (a) hard, malleable pavement
- (b) soft pavement
- (c) very hard pavement

(sample 52)

(sample 53)

(sample 54)

about n-C17 up; the hard, malleable pavement contains resolvable n-alkane from n-C22 up (Type A); and the very hard pavement includes only UCM (Type B).

Discussion of "METULA" Results

A comparison of stranded oils collected 7 years after the wreck of the "AMOCO CADIZ" in Brittany, and 12½ years after the wreck of the "METULA" in the Strait of Magellan to the oil spilled experimentally on the beaches at Cape Hatt indicate that, whereas the Cape Hatt oil is weathering slowly, a direct time comparison cannot be made as none of the "AMOCO CADIZ" and few of the "METULA" samples include marker hydrocarbons.

If it may be assumed that any removal or weathering of the stranded oil will only occur during open water periods, some comparisons may be made. The number of open water months available for removal or weathering of oil at Cape Hatt by the sampling period in 1987 is estimated as between 12 and 15. This estimate is based on calculations from Dickins (1987), who reported open water for 2.5 months after the spill in 1981, 2 months in 1982, and 2 months in 1983. Assuming an average of two months open water per year since that year, the 1985 samples had been subjected to 8.5 open water months, whereas the 1987 samples have been exposed for 12.5 open water months. This figure could be as high as 14.5 months.

By comparison, when the samples were collected from the "AMOCO CADIZ" site, they had been exposed for 84 open water months, and the samples from the "METULA" site had been exposed for about 150 months.

The BIOS samples collected from the upper intertidal zone in Bay 11 indicate moderate weathering, whereas those from the mid-intertidal and lower intertidal zone indicate more advanced weathering. No samples are as weathered as those from the "AMOCO CADIZ" site, which have lost all n-alkane marker compounds and are made up of unresolved complex mixtures (UCM) of alkanes only. The only sample to include any resolved n-alkanes in the range n-C17 and up was a sample from a very low energy area 0.5 m below the spring high water mark (sample AMOCO CADIZ 12, Humphrey and Hope, 1986 page E-4). Unfortunately, no compositional traces made one year after the "AMOCO CADIZ" spill are available for direct comparison.

Most of the samples from the site of the "METULA" spill also are very weathered. There are, however, a number of samples identified as Type C in composition. These samples appear to be only as weathered as many of the BIOS samples. All such samples were collected from semi-terrestrial (at or above the spring high water mark) locations in the Strait of Magellan, and therefore should be compared to samples from BIOS backshore plots.

CONCLUSIONS

1. The oil-in-sediment concentrations on the BIOS backshore control plots at Crude Oil Point (T1 and T2) have changed little since 1980 and little weathering has taken place since 1985. Changes that have occurred in the total hydrocarbon analytical results from year to year may be considered artifacts of the sampling from sections of the plots with different sediment size distributions.

2. No pavement has formed on any sections of the backshore control plots. It can be assumed, therefore, that the processes which control the formation of an asphalt pavement are connected to the interaction of stranded oil with (sea) water, probably through the formation of a hard surface crust.

3. Oil remains on the Bay 11 intertidal zone, although 85% of the beach is now visually clean after just over one year of cumulative open water conditions (in 1981 only 42% of the intertidal zone was visually clean). The oil cover and the total volume of remaining oil continued to decrease when compared to previous surveys.

4. The asphalt pavement is the dominant feature of the Bay 11 oil cover and accounts for approximately 60% of the remaining oil, although it has an area of only 220 m² out of a total oil cover of 2240 m². The area of the pavement did not decrease between 1985 and 1987, although physically the pavement was soft compared to 1983 and 1985 observations.

5. Total hydrocarbon concentrations remain high in the Bay 11 pavement samples (mean 16,200 mg kg⁻¹) and those samples with high oil concentrations remain relatively unweathered. Areas that were considered to be visually clean, such as the mid-beach trough, were found to contain oil with oil-in-sediment concentrations of the order of 2000 mg kg⁻¹ (0.2 to 0.4% by weight).

6. It has become evident that the visual and chemical observations generally support each other. This has an important implication as it means that observations and data from other studies, such as the "AMOCO CADIZ" and "METULA" site visits, can be used with a degree of confidence for comparison with the BIOS results.

7. The samples from the asphalt pavements of the "METULA" spill area show that (a) high oil concentrations (up to 50,000 mg kg⁻¹, 5% by weight) remain after 12½ years and (b) there are a range of weathered oil types, with some being relatively unweathered whereas other pavement samples contain predominantly UCMs. Higher oil concentrations are evident from sand sediments whereas lower concentrations are associated with sand-cobble material.

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TEST AND EVALUATION OF A NEW AND UNIQUE
FIRE CONTAINMENT BOOM

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ABSTRACT

During the fall of 1987, a new concept for fire containment boom was evaluated during burn tests in Hastings, Minnesota, and in Kenai, Alaska. The 3M Company used specially fabricated, high-temperature ceramic materials to develop a curtain boom with semi-solid flotation. The fire containment boom was designed to appear and function as a conventional boom with a sacrificial outer layer covering its internal fire-resistant components. Test sections of boom with a cylindrical buoyancy component 10 inches (25.4 centimeters) in diameter were formed into closed loops and subjected to a continuous flow of oil (heptane and Prudhoe Bay crude). The oils were ignited exposing the test booms to peak flame temperatures typically between 1400°F and 1800°F (800°C and 1000°C). Following tests with total exposures of 6 hours (with heptane) and 24 hours (with crude oil), the booms were found to have minimal thermally induced degradation of their ceramic components and no degradation of their primary structural members above and below water. The burn tests and subsequent sea trials in Port Canaveral, Florida involving 500 feet (152 meters) of fire boom reveal that the boom will survive prolonged exposures to burning oil and that the boom has good sea-keeping and oil-containment characteristics while under tow in light seas. This project has provided important information leading to the development of a unique oil spill containment barrier for controlling an accidental fire or for enhancing a deliberate attempt to burn oil in situ.

BACKGROUND

During the past decade, several groups have seriously considered the elimination of spilled oil through in-situ burning (Batteille, 1979; Buist, 1987; Evans et al., 1987; Industry Task Group, 1983; Shell et al., 1983; and Smith and Diaz, 1985). Much of this work has demonstrated that large volumes of oil can be removed from a water-borne spill quickly and efficiently (Shell et al., 1984; Allen, 1987). The success of any in-situ burning operation, however, is strongly dependent on the flammability (or ease of ignition) of the oil and upon the oil's thickness during burning. It is essential, for example, that burning oil be maintained at a thickness of at least a tenth of an inch (2 to 3 millimeters) to sustain efficient combustion. Even under arctic conditions, such oil film thicknesses generally require the use of a fire-resistant barrier that can be used to completely encircle the spill or be used in conjunction with winds and/or currents to herd the oil into a limited containment zone.

A companion paper, "Comparison of Response Options for Offshore Oil Spills," (Allen, 1988) in these seminar proceedings deals with specific modes of use for a fire containment barrier. The reader is urged to examine that paper for operational considerations that 3M used in selecting materials and in designing a fire-resistant containment barrier. It was understood, for example, that under most conditions the deliberate elimination of spilled oil through burning should be used only after every mechanical removal technique available had been considered. In addition, it was hoped that such a floating barrier might prove to be an effective "fire break" in situations where an accidental petroleum fire might otherwise spread on water to neighboring vessels or facilities.

DESIGN AND PHYSICAL CHARACTERISTICS

The objective of the fire boom development program was to utilize the unique ceramic materials technologies of 3M to design a functional conventional curtain boom able to survive intense, long-duration burns.

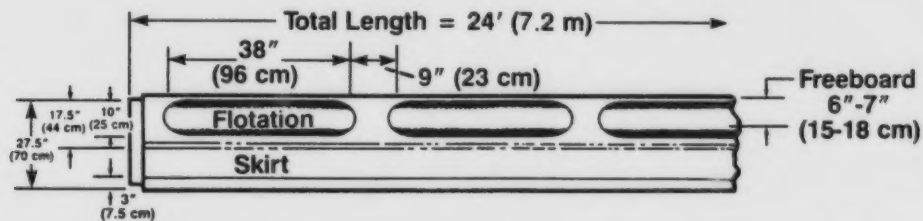
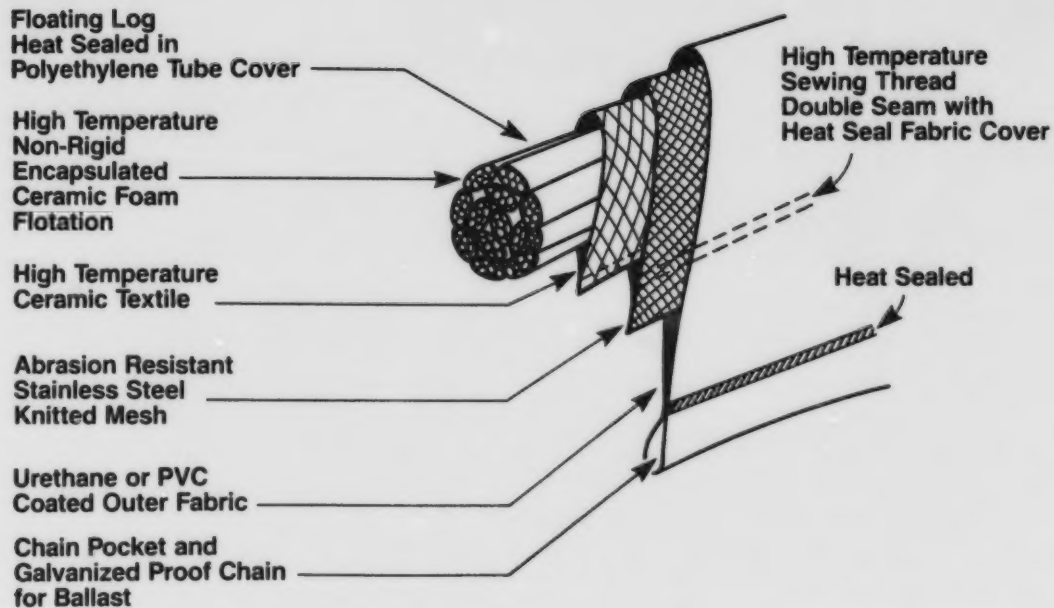
The results of numerous experiments and prototype tests led to the current 3M Fire Boom design. As shown in Figure 1, the 3M Fire Boom consists of a high-temperature, closed-cell ceramic foam held inside lineal pockets of stainless steel mesh. The foam-filled pockets (or cells) are combined to form a float log, which is covered with a heat-sealed polyethylene bag. The flotation logs are then covered with a layer of specially designed Nextel ceramic fabric. A layer of stainless-steel knitted-wire mesh is then positioned between the ceramic fabric and a surface layer of PVC-coated fabric similar to that used on conventional oil containment booms. The tension member is a 1/4-inch (6.35-millimeter) galvanized proof-coil chain held within a double-fabric chain pocket to improve abrasion resistance. Sections of boom are joined using standard Universal™ connectors.

The boom configurations used during this phase of the development program involved two boom sizes: one with flotation sections 10 inches (25.4 centimeters) in diameter, weighing approximately 6-1/2 pounds per foot (3 kilograms per meter), and another 12 inches (30.5 centimeters) in diameter, weighing approximately 10 pounds per foot (4-1/2 kilograms per meter). 3M is currently working to reduce these weights considerably.

BURN TESTS

Six-Hour Exposure Test with Heptane

The six-hour burn test was conducted at the 3M Fire Training Center in Hastings, Minnesota, during September, 1987. The boom was 28 feet (8.5 meters) long, with a flotation diameter of 10 inches (25.4 centimeters). Each flotation log was approximately 38 inches (97 centimeters) long, with a 12-inch (30.4-centimeter) skirt. Thermocouples were attached at key points on the boom and on a pole at the center of the burn area approximately 8 inches (20 centimeters) above the water line (Figure 2). A continuous flow of heptane was fed to the burn area at a rate of about 1 gallon per minute (3.8 liters per minute) and then ignited (Figure 3). Thermocouple readings were recorded, with maximum temperatures exceeding 1500°F (815°C). After the test the boom was examined for fabric and mesh flexibility, fabric and seam strength, and float pocket integrity. Final inspections of these



Universeal™ Connector used on Fire Boom slide type connectors held in place with dual locking pins.

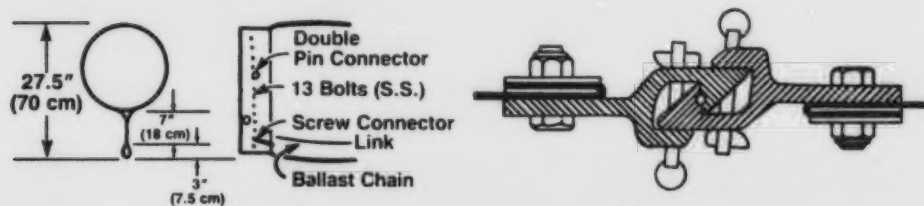


FIGURE 1 3M FIRE BOOM CONFIGURATION DURING KENAI TEST, OCTOBER, 1987

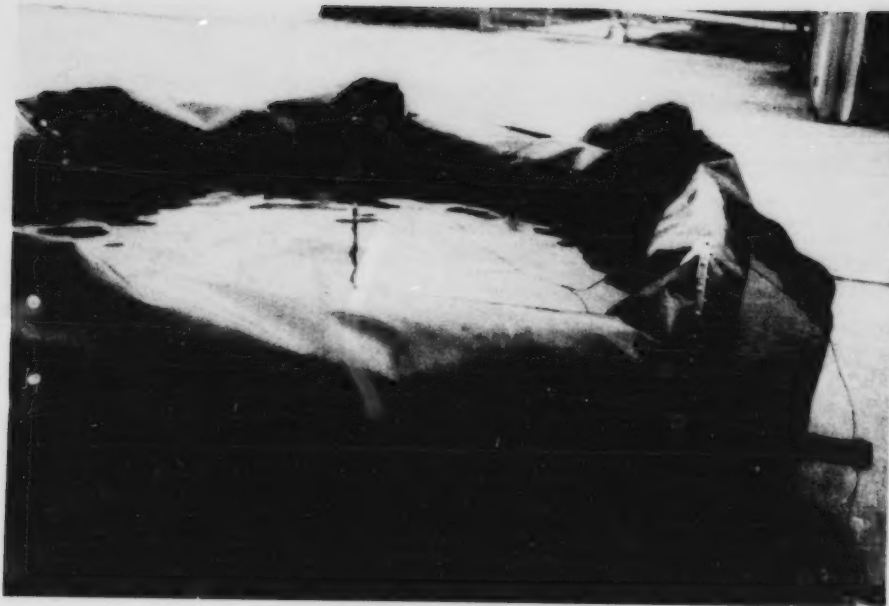


FIGURE 2 FIRE BOOM PRIOR TO 6-HOUR HEPTANE BURN TEST IN HASTINGS, MINNESOTA



FIGURE 3 FIRE BOOM AFTER IGNITION OF HEPTANE IN 6-HOUR BURN TEST

components revealed no sign of thermal stress, and lab testing of the fabrics showed very little loss of original strengths.

24-Hour Exposure Test with Crude Oil

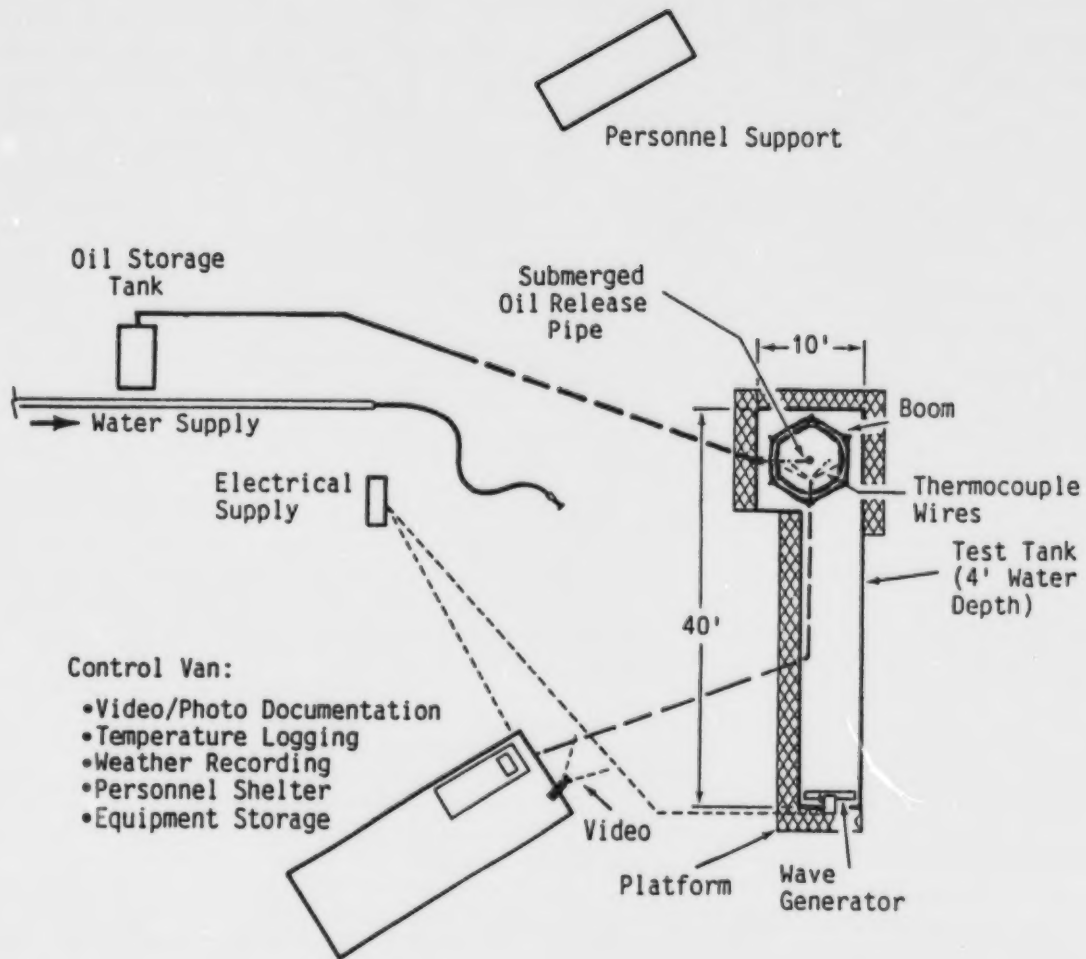
Objectives: The primary objective of the 24-hour test burn at Kenai, Alaska (October, 1987), was to evaluate the performance of the 3M Fire Boom during and following prolonged exposure to burning crude oil. The test included evaluations of internal as well as external resistance to fire; impermeability to oil before, during and following exposure to flame; structural integrity against tensile forces, bending motions and abrasion; and the ease with which the boom could be handled and transported before the burn and at its conclusion. Other assessments included the boom's freeboard before, during and after the burn, its resistance to impact with a sharp object (following 24 hours of exposure to fire), and its potential for reuse.

Location and Facilities: The test burn was conducted at the Kenai Community College Fire Control Training Center in Kenai, Alaska. Figure 4 illustrates the basic layout for test equipment and support facilities at the burn site. Mobile equipment was moved to the site for weather protection and to accommodate various storage and documentation needs. Approximately 2,000 gallons (7,500 liters) of Prudhoe Bay crude oil were stored on site and used during the 24-hour burn test. The crude oil was allowed to gravity-feed into a 1-inch (2.54-centimeter) pipe that provided a continuous flow of oil to the center of the boomed containment area in the test tank.

Test Procedures: The 3M Fire Boom used during this test had a flotation diameter of 10 inches (25.4 centimeters) and a total length of approximately 24 feet (7.3 meters). The boom was closed into a hexagonal shape within the 10-foot (3-meter) square portion of the test tank (Figure 5). The sacrificial layer used during this test was made of Urethane (23 ounces per square yard, or 780 grams per square meter); however, a second test was conducted later in the week using a PVC layer of the same weight. The tests included both materials in response to requests from potential Fire Boom users regarding their own preferences for an outer covering.

Single flotation logs nearly 3-1/2 feet (1 meter) long were used as flotation in the test boom in order to accommodate a closed loop of Fire Boom in the test tank. And, because of the amount of outer fabric needed to form a small closed hexagon, each log was separated by a fold (or pleat) of material that would not be necessary in any final boom configuration.

Before the 3M Fire Boom was set in the test tank, thermocouples were positioned at six locations on the boom and at four locations above and below water in the tank. The boom was then lifted into position within the tank so that the oil feed pipe was at the center of the area enclosed by the boom. Small subsurface wires held the boom in position to prevent winds from moving the boom away from the source of oil and to maintain the boom's orientation within the tank. Thermocouple wires were fed into the documentation van and connected to a multi-channel digital thermometer and scanner system. Temperatures at each thermocouple were logged frequently during the early stages of the burn and then at 15-minute intervals throughout the rest of the test.



Fire Containment Boom Test Facility

Location: Kenai Community College Fire Control Training Site, Kenai, Alaska

Test Tank: 40-ft long, 5-ft-high steel tank with 10 ft x 10 ft area for placement of boom.

FIGURE 4 KENAI, ALASKA, TEST FACILITY

Throughout the test burn, crude oil was fed to the contained area at between 1/2 and 1 gallon per minute (1.9 to 3.8 liters per minute). This flow rate provided sufficient oil for a continuous burn of the crude oil over one-half to three-quarters of the area within the boom. The resulting fire and boom performance were recorded using still photography (color slides) and two video cameras. Photo and video documentation was collected at the beginning and end of the test, at brief shutdowns of the fire for close-up inspection, and at one-hour intervals throughout the burn.

Throughout the test burn, air temperatures were typically between 32°F and 40°F (0°C and 5°C) at night, and between 40°F and 50°F (5°C and 10°C) during the day. Visibility remained good, with scattered clouds and intermittent light breezes of 0 to 3 miles per hour (0 to 1-1/2 meters/second). No rain fell during the 24-hour test burn.

Burn Test Results: Figure 6 shows the nature of the fire approximately one minute following ignition. Much of the outer, sacrificial (Urethane) layer is still in place on the side of the boom facing away from the fire. In Figure 7, several minutes later, the last portion of the sacrificial layer can be seen burning down to the water line.

During this early ignition stage and throughout the remainder of the test burn, peak flame temperatures were typically in the 1200°F to 1650°F (650°C to 900°C) range, with occasional excursions above 1800°F (1000°C). Depending on the wind and the nature of oil/residue accumulation within the boom, the location of the peak temperatures shifted around the fire containment area. Sometimes the fire would drop back to a fairly small burn area for a few seconds while fresh, cold crude oil would



FIGURE 5 FIRE BOOM IN POSITION PRIOR TO IGNITION OF CRUDE OIL

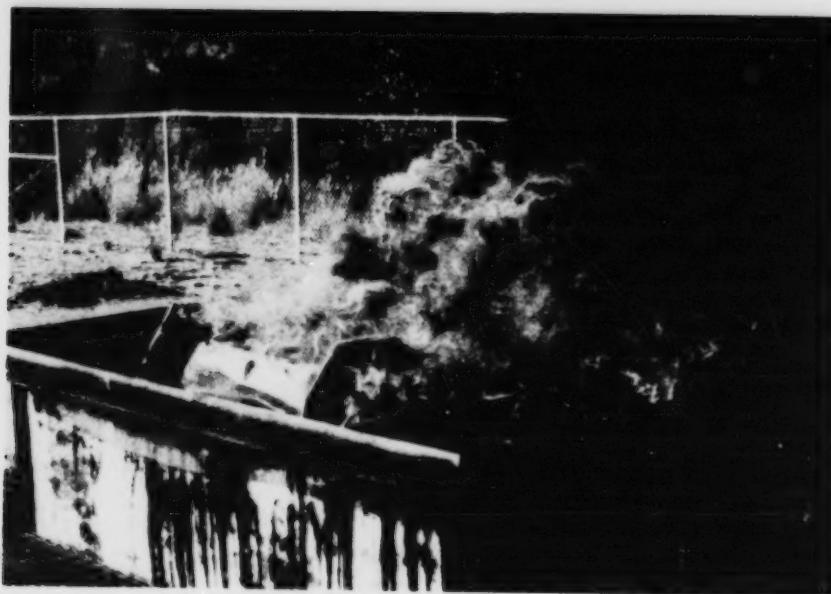


FIGURE 6 3M FIRE BOOM WITH BURNING OIL APPROXIMATELY 1 MINUTE FOLLOWING IGNITION OF THE OIL



FIGURE 7 CLOSEUP VIEW OF THE FIRE BOOM AS THE LAST PORTION OF THE SACRIFICIAL LAYER IS BURNED OFF

bubble up and spread a few feet from the fire. The oil would heat up rapidly and release vapors that would then ignite and cause a rapid spread of intense fire over the entire containment area. This natural oscillation of burn size and intensity was noted throughout the test to be somewhat dependent on the temperature of the water directly beneath the fire.

One hour into the burn, the supply of oil to the test tank was shut off, thus allowing the fire within the boomed area to gradually go out. When it was safe to inspect the boom up close, it was apparent that the sacrificial layer was completely removed (as expected) on all sides of the boom above water. All other components of the boom appeared to be in excellent condition. The wire mesh and Nextel fabric were still quite strong and pliable. Figure 8 shows a close-up view of the boom with remnants of charred urethane and burned oil residue in small patches on the side of the boom facing away from the fire. The average freeboard of the boom was measured at between 6 and 7 inches (15 and 18 centimeters), approximately an inch (2 to 3 centimeters) less than the boom's freeboard prior to ignition. Such reduction in freeboard was expected since the removal of the outer sacrificial layer (supported by air captured inside) could no longer contribute to the overall freeboard.

Within a few minutes, the flow of oil to the boom was once again begun and the oil was ignited. As during the first hour of the test burn, a constant exposure to burning crude oil was established using the same feed rate. At times the intensity of the burn increased noticeably as water began to boil directly beneath the burning crude oil. Such boiling resulted in small eruptions of water vapor as bubbles began to form and build in pressure beneath the layer of oil. When the oil layer was sufficiently



FIGURE 8 CLOSEUP VIEW AT THE 1-HOUR INSPECTION SHOWING THE SAME CORNER OF THE BOOM SEEN IN FIGURE 7

thick to require high pressures for vapor release, the eruptions blasted particles of hot and/or burning oil into the air. These particles substantially increased the size and intensity of the burn, resulting in the splattering of some oil onto the water surrounding the boom. Such splattering will likely be reduced in an actual open-water burn since moving subsurface waters will tend to disperse the heated water beneath the fire into the cooler water below.

Once again, at six hours into the burn test, the flow of oil to the test tank was stopped and the boom was examined. The condition of the boom during this inspection was basically as observed and described following the one-hour burn period. There were no signs of deterioration anywhere in the stainless steel mesh surrounding the flotation and ceramic (Nextel) fabric of the boom. The ceramic fabric was discolored in places where it had been exposed to the most intense and prolonged heat; however, the fabric was still pliable and showed no visual signs of significant thermal degradation.

Again, within a few minutes following the brief inspection of the boom, a continuous flow of oil was re-ignited and allowed to burn for several more hours. At approximately half way through the planned 24-hour exposure, it was decided that the fire would be shutdown for approximately 12 hours. It was felt that such a cooling-down period, followed by additional fire exposure, would be a realistic and important test that a fire containment boom might actually experience under real-world conditions.

Following the deliberate cooling down of all boom components, the flow of oil and ignition was once again initiated. Throughout the second half of the burn test, the boom looked and performed as it had during the first half. Though exposed to prolonged extreme temperatures and then cooled to near freezing, the boom remained flexible, impermeable and resistant to repeated exposures to burning oil.

Upon completion of the 24-hour exposure period, the Fire Boom was allowed to cool and then removed from the test tank. The boom was quite capable of taking the usual bending and twisting motions associated with such handling. It was also observed that there was no noticeable reduction in the resistance of the boom's wire mesh to abrasion. In fact, personnel on site could not tear or break the wire mesh with gloved hands. It was only with an axe that a small hole was produced through the wire mesh. Enlargement of the hole revealed that only one of the cells containing the foamed ceramic material was broken open as well. A second blow with the axe did open another cell; however, when picked up and shaken, the entire flotation section released only a small amount of foam material from two of the 14 flotation cells. It appeared that while a sharp object could puncture the boom, such damage would not normally result in a catastrophic failure of the boom. It is very likely that the boom could have continued to maintain its freeboard, its impermeability to oil and its resistance to fire following the deliberate damage done to it.

Further inspection of the boom included a complete removal of one flotation section and a careful examination of the boom's below-water components. The flotation section removed was that which had been hit earlier with an axe. It was quite evident that those cells which had not been deliberately cut open were in excellent shape and that the ceramic float had suffered no apparent degradation of any kind. Examination of the below-water components also revealed that the boom remained impermeable to oil at and below the water line.

A second test was carried out a few days later with burning crude oil and a similar test boom, this time with a PVC outer sacrificial layer. All results were basically as noted for the earlier 24-hour burn; however, the PVC covering provided substantially more resistance to the fire. Even after many hours of exposure to the burning crude oil, the sacrificial PVC material remained intact several inches above the water line on the side of the boom facing away from the fire. This material provided an additional impermeable barrier against any movement of oil through the boom.

TOW TEST

Objectives

The primary objective of this phase of the program was to evaluate the performance of the 3M Fire Boom during full-scale deployment and towing operations. A boom 12 inches (25.4 centimeters) in diameter and 500 feet (152 meters) in length was used to obtain information on the boom's (1) ease of use, (2) roll and heave response during towing, (3) freeboard and susceptibility to splashover, and (4) general sea-keeping characteristics during conditions ranging from calm water to short-period wind chop.

Location

Port Canaveral, Florida, was selected as the tow test site. The Port Canaveral area offered excellent harbor facilities for deployment and for practice-booming of vessels, for towing in calm inland waterways, and for offshore operations as well.

Procedures

The packaging and transport of the Fire Boom to a boat-launching ramp at Port Canaveral was accomplished with a small flatbed truck and six workers. The same number of personnel were sufficient to deploy the 500 feet (152 meters) of boom from the truck and into the harbor. Two inboard workboats 25 feet (7-1/2 meters) in length were used for towing the boom, and a small 20-foot (6-meter) support boat was available for measurements, boom tending, and photographic work. Over a period of approximately 6 hours, the boom was towed by a single boat in a straight line at speeds up to 3 knots (1-1/2 meters per second) and by two boats in a U-configuration at speeds of 1/2 to 1-1/2 knots (0.25 to 0.75 meters per second).

During the towing operation, records were kept on tow-line tensions and boom performance. Underwater, surface, and aerial photographs were taken, while video coverage was obtained from the surface and the air. The boom's performance (freeboard, roll, heave, etc.) was assessed in natural sea states up to a light wind chop and in boat-generated waves of 2 feet (about 1/2 meter) while the boom was towed with and into the wind and waves.

During recovery of the boom, 14 men disconnected 50-foot (15.2-meter) sections at shoreline and carried them out of the water for draining, cleaning, and repacking on the flatbed truck. Observations and measurements were once again made on freeboard, ease of handling, susceptibility to abrasion/damage during recovery, and requirements for repacking and storage.

Results

Six workers and a single tow boat easily completed the deployment of 500 feet (152 meters) of Fire Boom from the storage containers and flatbed truck

(Figure 9). The entire length was deployed within 5 minutes, including the time required to complete the attachment of several connectors.

Once in the water, the boom was towed in a straight line toward one of the harbor's turning basins. The boom performed satisfactorily at several towing speeds. Measurements taken at several locations indicated a consistent freeboard of 10 to 11 inches (25.4 to 28 centimeters) at both flotation sections and at the boom's connectors. It should be recognized that the Fire Boom's freeboard following exposure to fire would be reduced by approximately 2 inches (5.1 centimeters).

In several tow tests with the boom in a U-configuration [typically with a 150-foot (46-meter) opening between the tow boats], the boom responded well to waves and to the currents generated by its own forward motion (Figure 10). At speeds of between 1/2 and 3/4 knot (0.25 and 0.75 meters per second), the boom's skirt and flotation chambers showed no signs of excessive roll. In addition, as waves (both natural and vessel-generated) came into contact with the boom, there were no indications of bridging or over-topping along the sides or apex of the boom's U-configuration (Figure 11). At speeds in excess of 1 knot (1/2 meter per second), there were the usual strong eddies behind the boom's apex that would normally be present with any boom. As expected, the tension recorded in the tow lines with normal swath widths and towing speeds remained between 200 and 400 pounds (890 and 1,780 newtons).

During all open-water towing tests, the boom demonstrated satisfactory sea-keeping characteristics based on close-up observations from the surface and from under water. The two comparably powered boats with 90-horsepower engines proved capable of carrying out all maneuvers that would normally be expected under actual spill conditions with the same boom length and comparable environmental conditions.

The recovery of the boom was completed using 14 people to lift one section (50 feet, or 15.2 meters) of the boom out of the water at a time. The recovery of the boom took approximately 40 minutes. The restowing of the boom on the truck for transport from the dock area required another 30 minutes. As in any actual spill situation, these recovery times are not excessive -- it is the deployment time (approximately 5 minutes with this boom) that would be most important.

SUMMARY

The 3M Fire Boom has been designed and constructed to function as a conventional bottom-tensioned curtain boom. While serving as a standard oil spill containment barrier, the boom can also be used as a fire-resistant barrier for the containment of burning oil on water. The internal components of the boom consist of high-temperature ceramic materials that are held in place and strengthened with stainless-steel wire mesh. The boom's outer PVC covering is intended as a sacrificial layer that would be at least partially removed along any section of the boom exposed to fire.

The Fire Boom has undergone full-scale tests during which contained heptane and crude oil layers have been burned with total exposures ranging from 6 hours to 24 hours. Tests have also been conducted with a full 500 feet (152 meters) of fire boom towed in varying configurations under calm-water harbor conditions to offshore seas involving short-period waves of one to two feet (approximately 1/2 meter). These tests revealed that the fire boom is capable of functioning as an effective containment barrier with



FIGURE 9 WORKERS DEPLOYING FIRE BOOM FROM FLATBED TRUCK INTO THE HARBOR



FIGURE 10 AERIAL VIEW OF FIRE BOOM WHILE UNDER TOW IN A U-CONFIGURATION

good wave-riding and towing characteristics. In addition, the boom is capable of surviving long-duration burns of oil contained and held against the barrier for extended periods of time.

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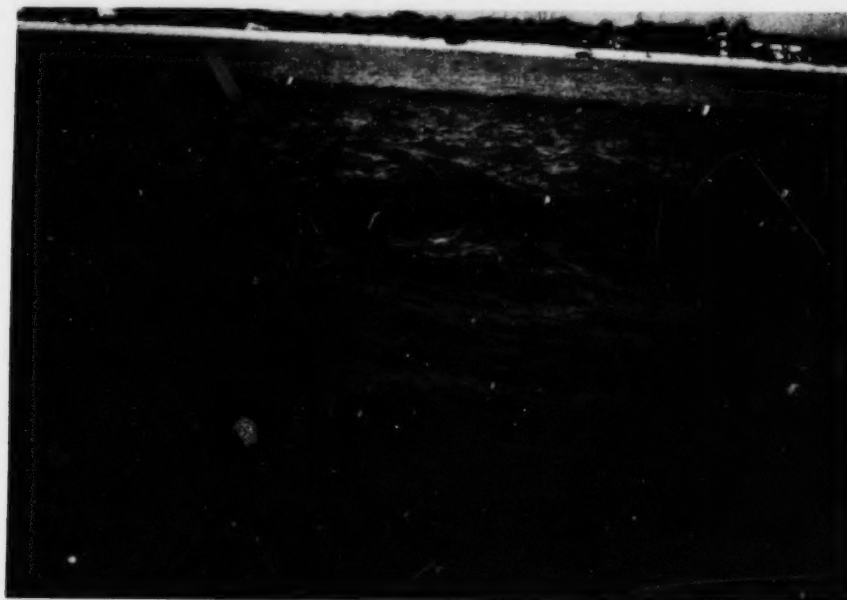


FIGURE 11 RESPONSE OF BOOM TO WAVES WHILE UNDER TOW

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Shallow Water Access Mop Platform (SWAMP)

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Abstract

Alaska Clean Seas has developed and evaluated a prototype skimming system for use in the shallow water environment between the shore and the barrier islands of the Alaskan Beaufort Sea.

Introduction

With the development of the Endicott field in the Alaskan Beaufort Sea east of Prudhoe Bay and with prospects for other near shore exploration and development in the area, Alaska Clean Seas saw a need for improved skimming capability for shallow water. This paper covers the design, development and testing of a skimming system to help meet this need.

Conceptual Development

Design specifications for the SWAMP include the points listed in the following sub-paragraphs:

- o Shallow Draft. To minimize draft and provide a stable work platform, conceptual development was based on a catamaran design. A commercially available welded aluminum pontoon system was selected to provide the basis for design.
- o Self Propelled. A conventional outboard engine installation was selected in order to minimize weight and provide flexibility in engine choice.
- o Self Contained Skimming System. A Centrifugal Systems Inc. model MW 62 rope mop engine and associated generator set were selected as a skimming system. It has been the experience of ACS and others involved with spill response in the Arctic that rope mops provide good performance and are versatile in application.
- o Weather Protection for Crew. In the arctic environment, good weather protection for the crew is essential for safety and efficiency.
- o Other Features. The vessel is provided with standard navigation lighting, a magnetic compass, attachments for ground tackle, railing for crew member safety, and radio

communication in the Marine VHF band and on UHF frequencies used by ACS for coordination of spill response operations.

Design

Specific aspects of the design are listed and discussed below:

- o **Floataction.** Two 27-ft (8.2-m) pontoons (Gregor Welded Boats Model A27 pontoons with bow shoes) were selected to provide buoyancy. The pontoons weigh approximately 230 lbs (104 kg) each, for a total pontoon weight of 460 lbs (209 kg). The total buoyancy of the two pontoons is estimated at 12,000 lbs (5,500 kg) in fresh water and 12,300 lbs (5,600 kg) in sea water. The total estimated weight of the vessel and crew with full tanks is 5,140 lbs (2,336 kg), for 133% reserve buoyancy.
- o **Deck.** The deck structure is designed to support the dead load of the mop machine and generator, plus a live load of 100 lbs per square foot (489 kg/m²), plus a maximum concentrated load of 200 lbs (91 kg) at any point. The main portion of the deck is 9'-6" (2.9 m) wide by 20' (6.1 m) long. Two 2' (0.6 m) by 6'-6" (2.0 m) catwalks extend forward, one on each pontoon. Deck joists are 4" (102 mm) by 1.580" (40.1 mm) aluminum channels spaced at 12" (0.3 m) intervals beneath the mop machine and the generator, and at 16" (0.4 m) intervals elsewhere. Decking is 3/16" (5 mm) aluminum diamond tread plate. Welded connections are used throughout, and the deck joists are welded to a pair of fore-and-aft rails on the top of each pontoon. The total deck weight is estimated at 1080 lbs (491 kg).
- o **Pilot House.** The pilot house was constructed from 1/8" (3 mm) aluminum plate. It is centered 24 in (0.6 m) forward of the rear edge of the deck. It measures 48" (1.2 m) fore-and-aft by 96" (2.4 m) wide by approximately 88" (2.2 m) high. Engine and steering controls are located in a console on the interior port wall of the pilothouse. A door is located on the starboard exterior side of the deckhouse. Walls are 1-1/2 inch (38 mm) thick. They are insulated with foam and lined with wood panelling. The entire pilothouse can be unbolted and removed, making it possible to load the vessel into a C-130 aircraft for transport to other locations. The weight of the pilot house is estimated at 515 lbs (234 kg).
- o **Engine and Engine controls.** A 70-hp (52-kW) outboard engine is provided, equipped with remote steering, throttle, gear shift and tilt controls. The engine weighs approximately 185 lbs (84 kg).

- o Mop Machine and Generator. The mop machine weighs 1400 lbs (636 kg). The generator which powers the mop weighs 1600 lbs (727 kg).
- o Rigging. An A-frame system is provided at the forward end of the vessel. This system can support the tail pulley for the rope mop system. As an alternative, the rope mop can be threaded through one or more tail pulleys attached to anchors placed forward of the vessel. A winch and pulley system is installed for use in raising and lowering the forward A-frame.

Construction and Evaluation.

The SWAMP was constructed by Alaska Clean Seas field personnel at the ABSORB operations center at Deadhorse Alaska. It was launched and it received preliminary testing in the waters around Prudhoe bay during late August 1987. It was used in connection with training exercises near the Endicott oilfield in early September, 1987. The vessel was found to handle well, and it moves comfortably through 2-ft harbor chop. (The vessel has not been operated under conditions more severe than this.) Its cruising speed in calm waters is 10 knots.

The SWAMP promises to be a useful addition to the Alaska Clean Seas spill response equipment inventory. Additional testing and design refinements are planned for the 1988 open water season.

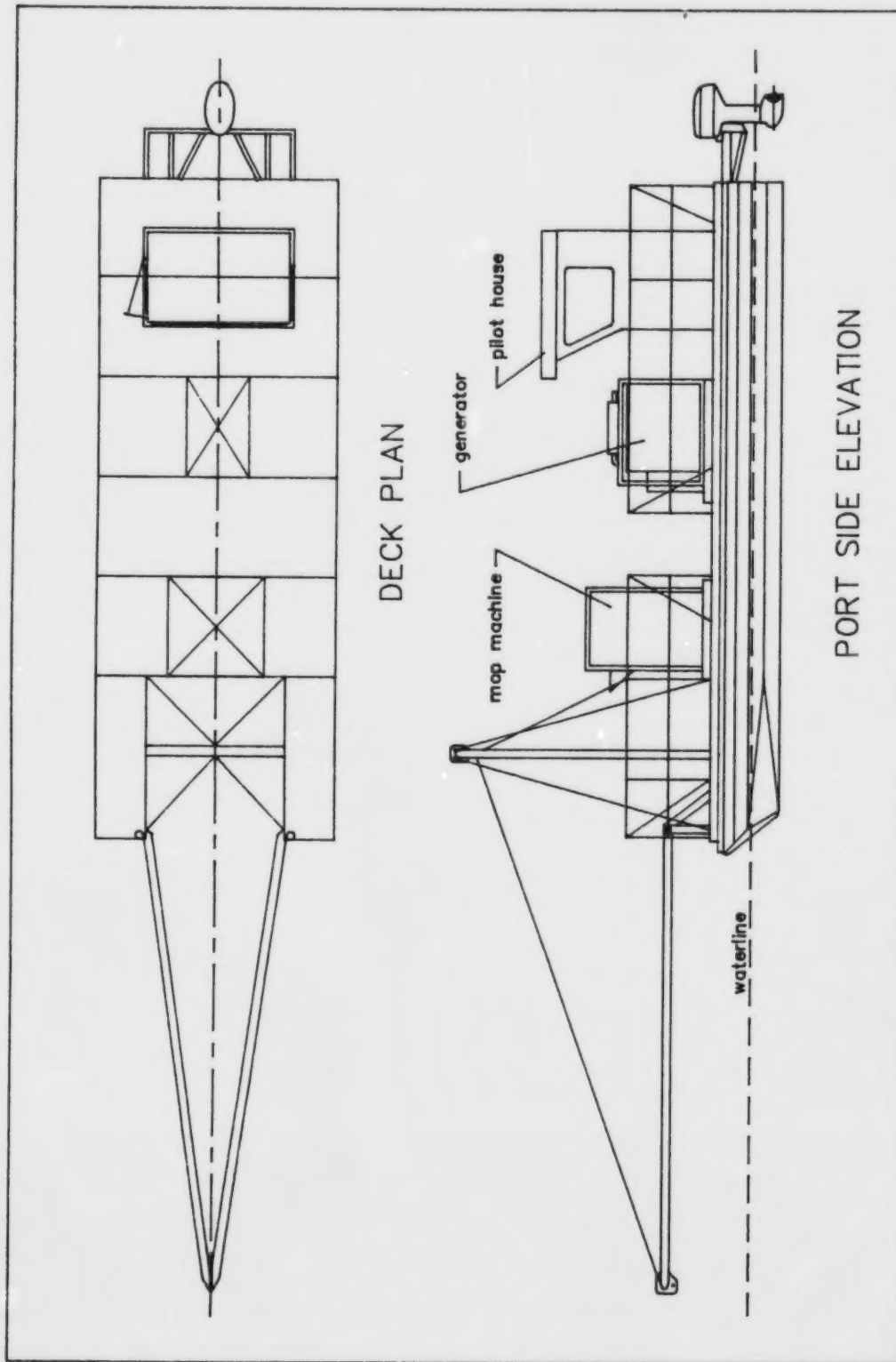


Figure 1. Shallow Water Access Mop Platform (SWAMP).

**ARCTICSKIM:
An Oilspill Skimming System for Broken Ice and Shallow Waters**

Richard V. Shafer, Alaska Clean Seas
Steve Bowen, Alaska Clean Seas

Abstract

Alaska Clean Seas has designed and constructed an ice deflection and skimming system which can be mounted on one of the organization's work boats. This system is intended for use in broken ice and in shallow near-shore waters of the Alaskan Beaufort Sea. It has been evaluated during spill response exercises conducted in September, 1987. Development of the system continues with an expanded version which will be ready for testing at Prudhoe Bay during the 1988 open water season. Performance of the system in a broken ice environment will be evaluated during early summer, 1988.

Introduction

The Endicott field, the first oil field to be developed in the Alaskan Beaufort Sea, lies about 20 km east of Prudhoe Bay and 4 km north of the delta of the Sagavanirktok River. The near shore area which might be affected by a spill at the Endicott production facility is very shallow, with depths ranging up to a maximum of about 2 m in the vicinity of the artificial islands where production facilities are located. With continuing petroleum exploration activity in the Alaskan Beaufort Sea environment, and with prospects for other nearshore development in the area, the need was seen for improved oilspill skimming capability for shallow water and where broken sea ice is present. This paper covers the design, development and testing of a skimming system to help meet this need. This project was undertaken by Alaska Clean Seas, a cooperatively funded oilspill response organization, on behalf of its participating companies.

Conceptual Development and Design

Design specifications for the ArcticSkim system include the points listed in the following subparagraphs. Figure 1 shows the configuration of the components and how they are attached to the vessel while in use.

- o Use with existing vessel. It was considered desirable to utilize an existing Alaska Clean Seas vessel as the principle component in the system. The North Star, a 10-m (32-ft) work boat was used for this purpose. Because the

North Star is an aluminum vessel, components of the skimming system were fabricated of aluminum wherever possible in order to minimize electrolytic corrosion.

- o Ice Deflection. An aluminum ice deflection frame was provided on the port side of the vessel. The forward end of the ice deflector frame is suspended from a push knee on the port bow of the vessel. It is attached by a pivot system which permits rotation of the forward end of the deflector frame about two axes: 1) a vertical axis, and 2) a horizontal axis perpendicular to the long dimension of the ice deflector frame. The aft end of the ice deflector frame is attached by a similar pivot system to a floating pontoon outrigger which is held away from the vessel by a system of articulated arms. (See Figure 1.) The ice deflector support system permits the elevation of the forward end to be adjusted vertically so that it is centered at the water line. The system of pivoting supports permits the outboard end of the ice deflector to move up and down, supported by the floating pontoon. In operation, the central axis of the ice deflector frame conforms generally to the water surface. Galvanized wire fence fabric is attached to the ice deflector frame to help screen out small pieces of floating ice.
- o Collection and Skimming System. Standard containment boom is deployed in a U-shaped configuration, with one end of the boom attached to the pontoon and the other end tied off to the side of the North Star. At the apex of this loop of containment boom a skimmer is provided. Various types of commercial skimmers might be utilized. For initial tests a Morris model MI-30 disk skimmer was employed.
- o Separation System. Fluid recovered by the skimmer is brought to a separation tank secured immediately forward of the deck house of the North Star. This tank provides for gravity separation of oil and water. A drain line and valve is provided at the bottom of the tank to allow for discharge of the water phase. The tank is also provided with an intake line, an oil discharge line and a flame control vent. Sight fittings on the tank wall permit observation of the level of fluid in the tank and the location of the oil-water interface.
- o Transfer and Storage System. An intake pump is provided to transfer fluid from the skimmer to the tank. A discharge pump transfers recovered oil from the separation tank to a floating bladder tank which is towed from the starboard side of the vessel.

Evaluation

The ARCTICKIM system was fabricated prior to the 1987 open water season. It was employed during spill response exercises conducted in early September, 1987. The system operated as intended. The outrigger and ice deflector were readily deployed and retracted by a crew of two men, and the vessel with deployed equipment was found to be reasonably maneuverable in spite of its asymmetrical configuration.

Continuing Development and Evaluation

Alaska Clean Seas is now fabricating a second outrigger and deflector system. The new components will be installed on the starboard side of the vessel. Together with the original components, they will comprise an expanded system which will have a more symmetrical configuration and approximately three times the swath width of the original. Alaska Clean Seas plans to test and evaluate the performance of the original and expanded versions of ArcticSkim in the presence of broken ice during early summer, 1988.

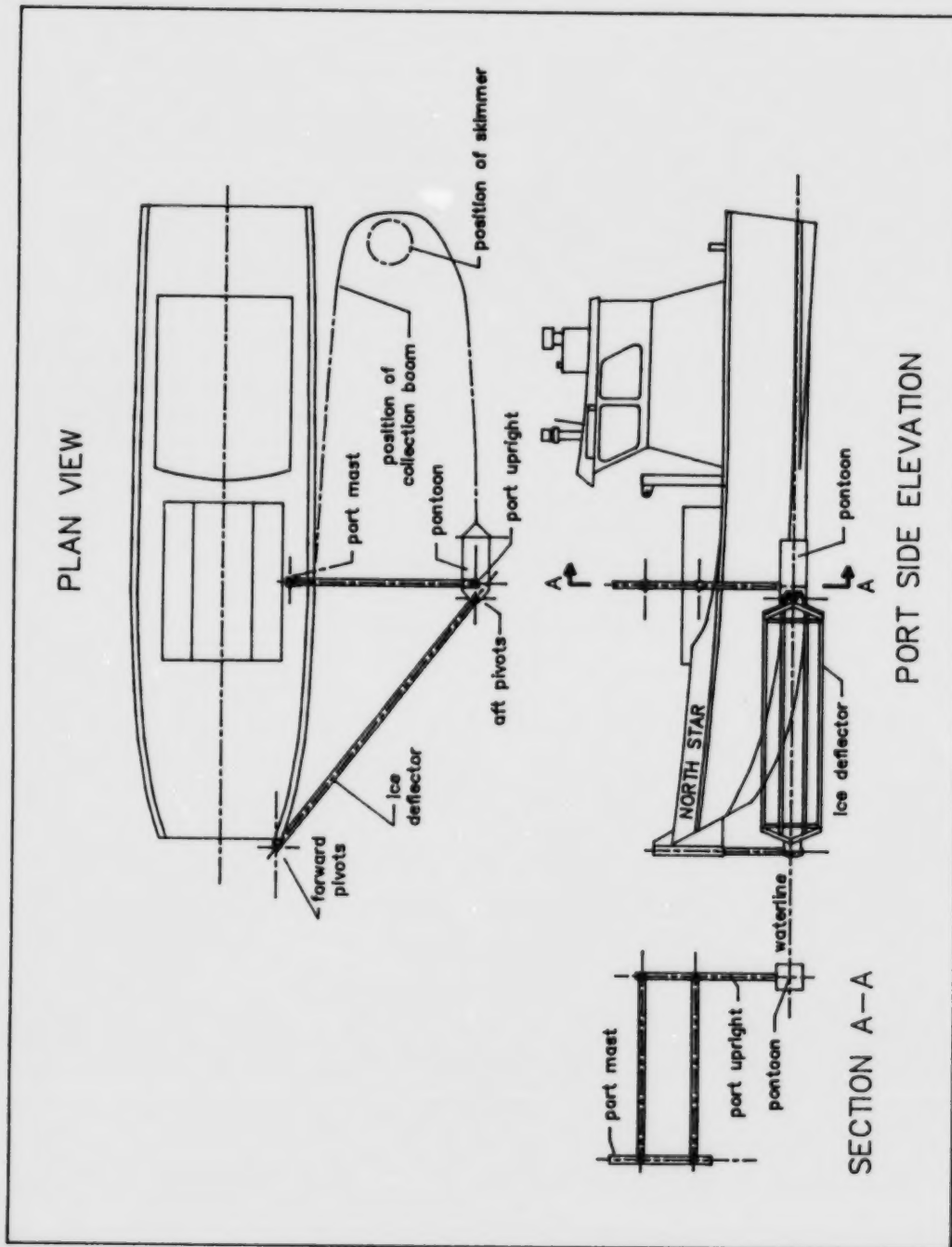


Figure 1. Arctic Skimming System.

CLEANUP AND CONTAINMENT OF A DIESEL
FUEL SPILL TO A SENSITIVE WATER BODY
AT A REMOTE SITE UNDER EXTREME WINTER CONDITIONS

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ABSTRACT

A spill of about 59,000 litres of diesel fuel occurred at a remote, unmanned generating facility about 165 km. north of Red Lake, Ontario in January of 1983. The spill was triggered by syphon action through a day tank vent. A large quantity of fuel escaped from a damaged containment dyke and made it's way under the snow to the water and ice surface of Warwick Lake.

Cleanup at the site began in late January of 1983 under extreme cold weather conditions (-35°C to -50°C). A further hindrance to cleanup was the fact that the site was only accessible by aircraft. Cleanup equipment was limited to that which could be transported by a DC-3 aircraft. Contaminated snow was collected and burned on site. Collection trenches were cut into the ice and fuel was recovered and burned. Cleanup work continued until late March 1983 by which time crews had recovered about 46,300 litres of fuel. A containment boom was sunk into the ice prior to ice break-up. Pockets of pooled fuel were burned off during ice break-up.

The clean-up at the site was considered successful and subsequent inspections of the area have shown that no significant damage to the local environment occurred.

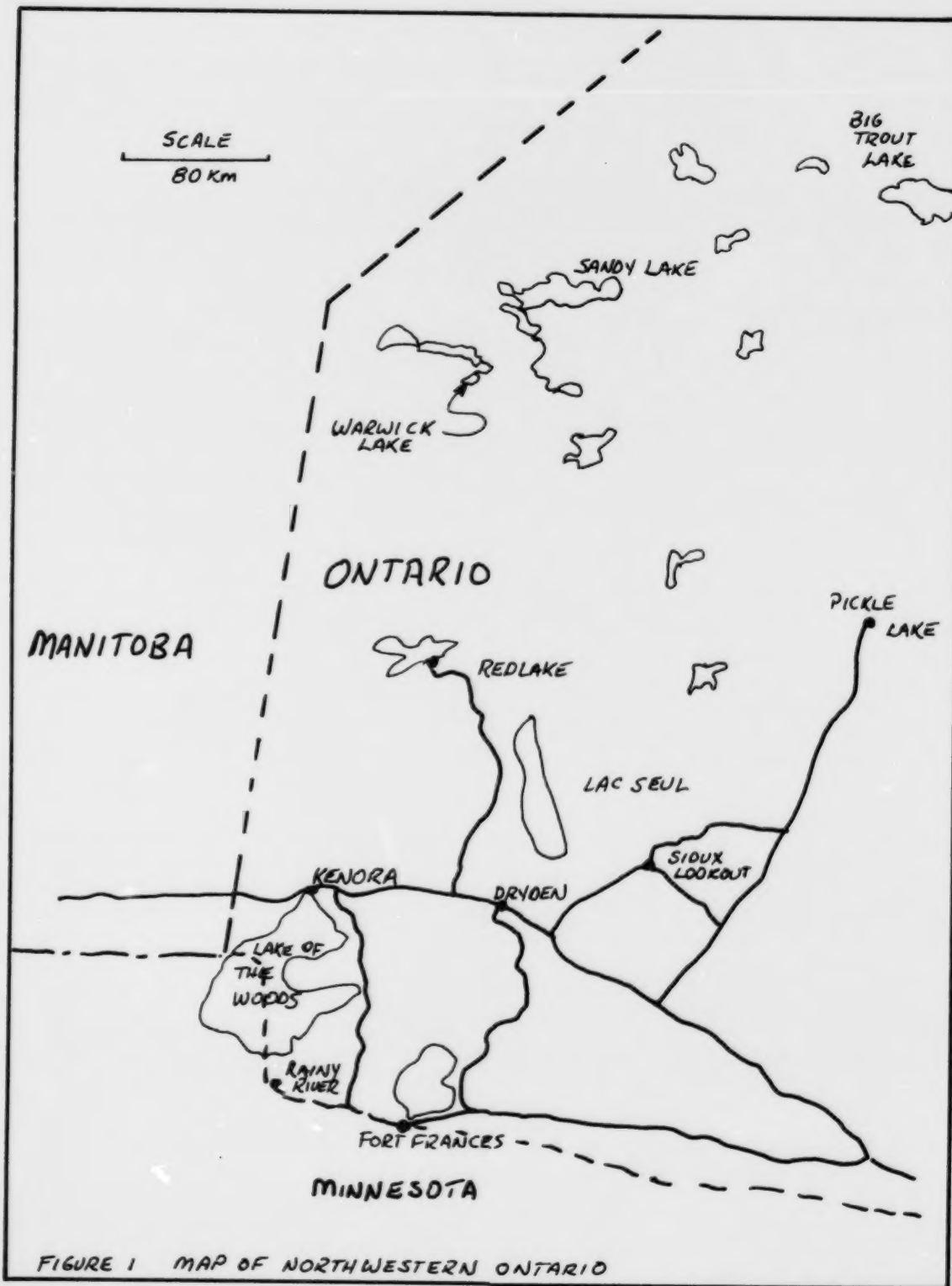
Introduction

Throughout Northern Ontario, Bell Canada operates a number of remote, unmanned telecommunication stations to provide communication links for remote communities. Because these sites are large distances from the hydro electric grid, power is supplied by on-site diesel powered generators. One of those sites is located on the shore of Warwick Lake.

Warwick Lake is located about 165 km north of Red Lake. The lake has a surface area of about 1550 hectares and is part of the McInnes Lake/Deer Lake chain which feeds the Severn River watershed. Access is by air only and although it is remote, one fishing outpost cabin, one trapper's cabin and a Bell Canada relay tower and station are located on the lake. Figure 1 is a map of Northwestern Ontario showing the location of Warwick Lake.

Ecological Aspects of Warwick Lake

A 1978 survey by the Ontario Ministry of Natural Resources found the



mean depth of the lake to be 7.6 m with the maximum recorded depth of 29.5 m. The lake is fed by two main inflows. The one outlet from the lake has a recorded mean outflow of 6.48 cubic metres per second.

At the time of the survey the lake had a sechhi disc reading of 2.6 m, a mean surface pH of 7.0 and dissolved oxygen readings near saturation levels. Only 10.4 hectares of aquatic vegetation was noted.

The survey noted 15 beaver lodges on the lake. A wide variety of sports fish, coarse fish and food fish species were netted during the survey. Sports fish included pickerel, sauger, whitefish, and northern pike. Coarse and food species included burbot, sucker, perch and shiner. Lake conditions would support a lake trout fishery, although no lake trout were netted during the survey.

The Bell Canada Station

The Bell Canada relay tower and telecommunication station at Warwick Lake consists of a diesel-powered generating station (located in the diesel buildings, see Figure 2), two 32,000 litre diesel storage tanks, an accommodation building, a storage shed, and a relay tower.

The storage tanks and generator are located on the side of a low hill about 45 m upslope from the shore of the lake. A containment dyke was constructed from local clay material downstream of the tanks and generator house.

Fuel is delivered to the site via cargo aircraft, usually DC-3, during the winter. Deliveries are only made during the winter because float equipped aircraft have limited payloads, whereas a wheel/ski equipped DC-3 can deliver up to 4500 litres per flight. The frozen lake surface provides the aircraft with a ready-made runway.

Fuel storage facilities are usually sized to accommodate about 2 years fuel consumption. This is necessary to ensure that fuel is always available since bad ice conditions could preclude fuel delivery for an entire winter.

Fuel is pumped from the aircraft by a portable fuel pump through a length of supply hose to a quick-connect fitting at the fuel control cabinet. Since the site is unmanned, fuel deliveries are usually made by the pilot without any Bell Canada personnel in attendance.

Discovery of the Spill

On January 16, 1983 a Bell Canada technician was flown into Warwick Lake to perform routine maintenance on the diesel generators. At that time, he discovered a large quantity of diesel fuel in the containment area below the generator building. He also noted that both storage tanks were nearly empty with only about 2,300 litres remaining in each. The technician made an inspection of the system to determine the source of the apparent loss. During his inspection he found that the valve to the diesel building heater storage tank was open. He concluded that the fuel had fed to the storage tank and overflowed through the tank vent.

Spill Evaluation

On January 17, 1983, Bell Canada notified the Kenora District Office of

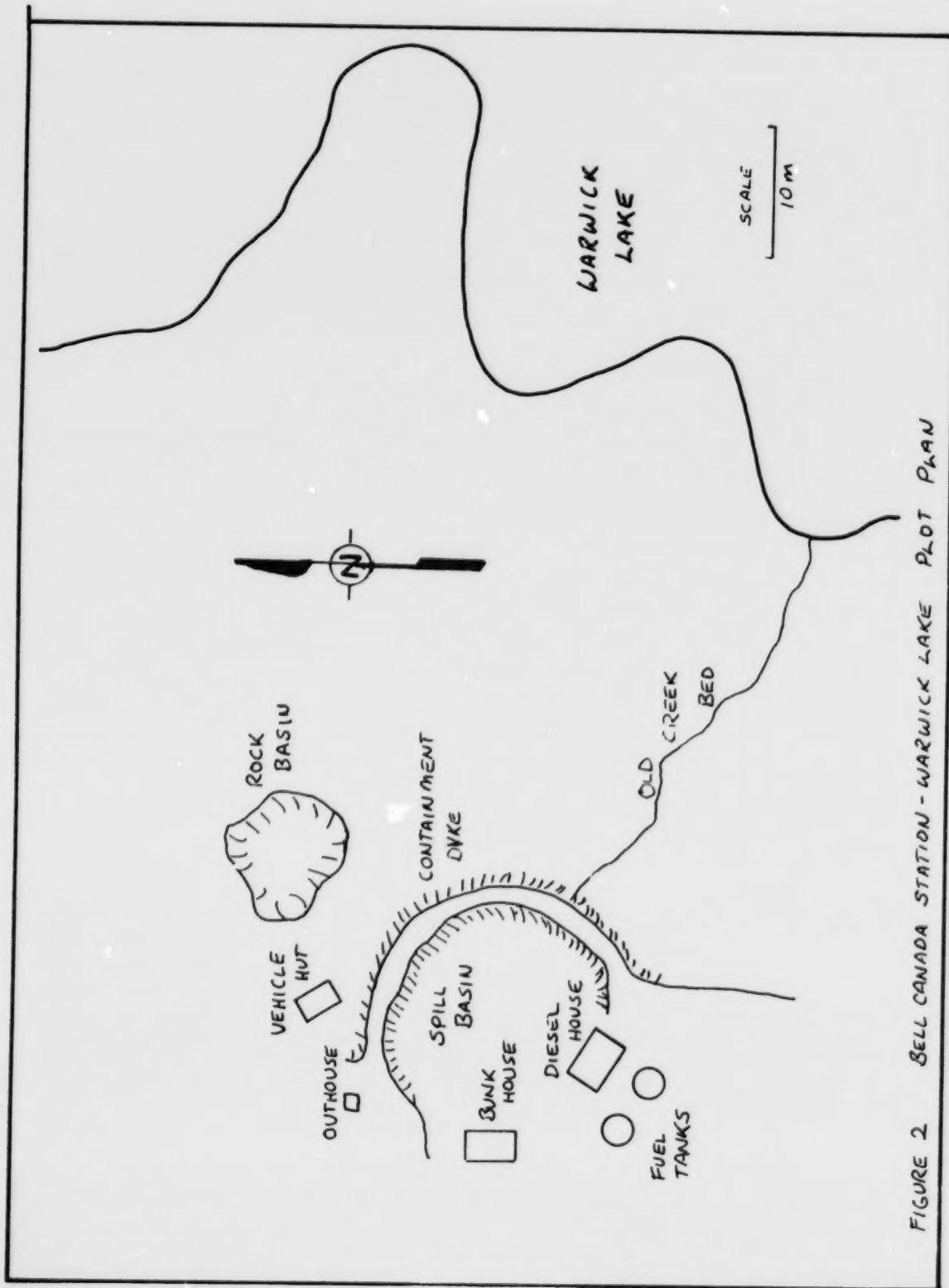


FIGURE 2 BELL CANADA STATION - WARWICK LAKE PLOT PLAN

the Ontario Ministry of the Environment (MOE) of the spill. After assessing the information provided, two officers from the Kenora MOE office made arrangements to fly to the site the following day to meet with representatives of Bell Canada and determine a cleanup plan.

On the morning of January 18, 1983 the two MOE officers flew out of Kenora on an Ontario Ministry of Natural Resources (MNR) Turbo Beaver. After a refueling stop at Red Lake the aircraft made its way to Warwick Lake and set down on the ice at about 11:30 a.m. On shutting the aircraft down the pilot indicated that the inspection would have to be made as quickly as possible because the outside temperature was -47°C . The pilot was concerned that he would not be able to restart the aircraft if it was shutdown for an extended period of time.

After a quick discussion with the Bell Canada representative, the officers made a detailed inspection of the site. The first area inspected was the diesel building. A large quantity of fuel was trapped behind the dyke below the diesel house. On closer inspection it was discovered that a portion of the dyke had been worn away, possibly by erosion, and had allowed the fuel to escape the protection dyke. A trail of fuel about 1-2 metres wide was followed beneath the snow to the surface of the lake along what appeared to be an old creek bed. Because of the depth of snow (about 1 m) it was difficult to determine the actual extent of the spill, however it appeared that the fuel had flowed out onto the ice surface (see Figure 3). The area of ice contamination appeared to extend about 15 m out from the edge of the lake about 50-65 m wide. It did not appear at that time that the fuel had gone beneath the ice.

In all contaminated areas downstream of the dyke the lower 15 cm of snow had acted as an absorbent, soaking up the fuel. On the shore portion of the spill, the fuel had not penetrated the ground frost. On the lake portion of the spill, ice conditions were such (few pores) that very little, if any, fuel had penetrated the ice.

Following the survey of the spill site, a closer examination of the diesel house and fuel delivery system was made. The fuel storage facilities consisted of 2 vertical 32,000 litre steel storage tanks connected by a load levelling line. Distribution lines from these tanks fed the day tanks for the two diesel generators housed in the generator building. One of the distribution lines also fed an exterior 450 litre storage tank which supplied the generator building space heater. The other line fed a storage tank for the bunkhouse space heater. Figure 4 shows the plan and elevation schematics of the distribution system. It was noted that the loop on the generation house heater storage tank vent extended back down to the ground and was not terminated after a few centimetres, as is normal.

From the information that was provided by Bell Canada and from observations of the site it was confirmed that the source of the spill was the space heater tank vent. The valve feeding the heater storage tank had been opened to fill the tank. After the tank was filled, the valve was left open. Some time previous to the discovery of the spill the large storage tanks were filled. It appeared that during the filling of the large tanks the level in the tanks was raised above the top of the heater storage tank vent loop and fuel was forced by gravity through the vent. This created a syphon action which in turn drained about 59,000 litres of diesel fuel from the tanks.

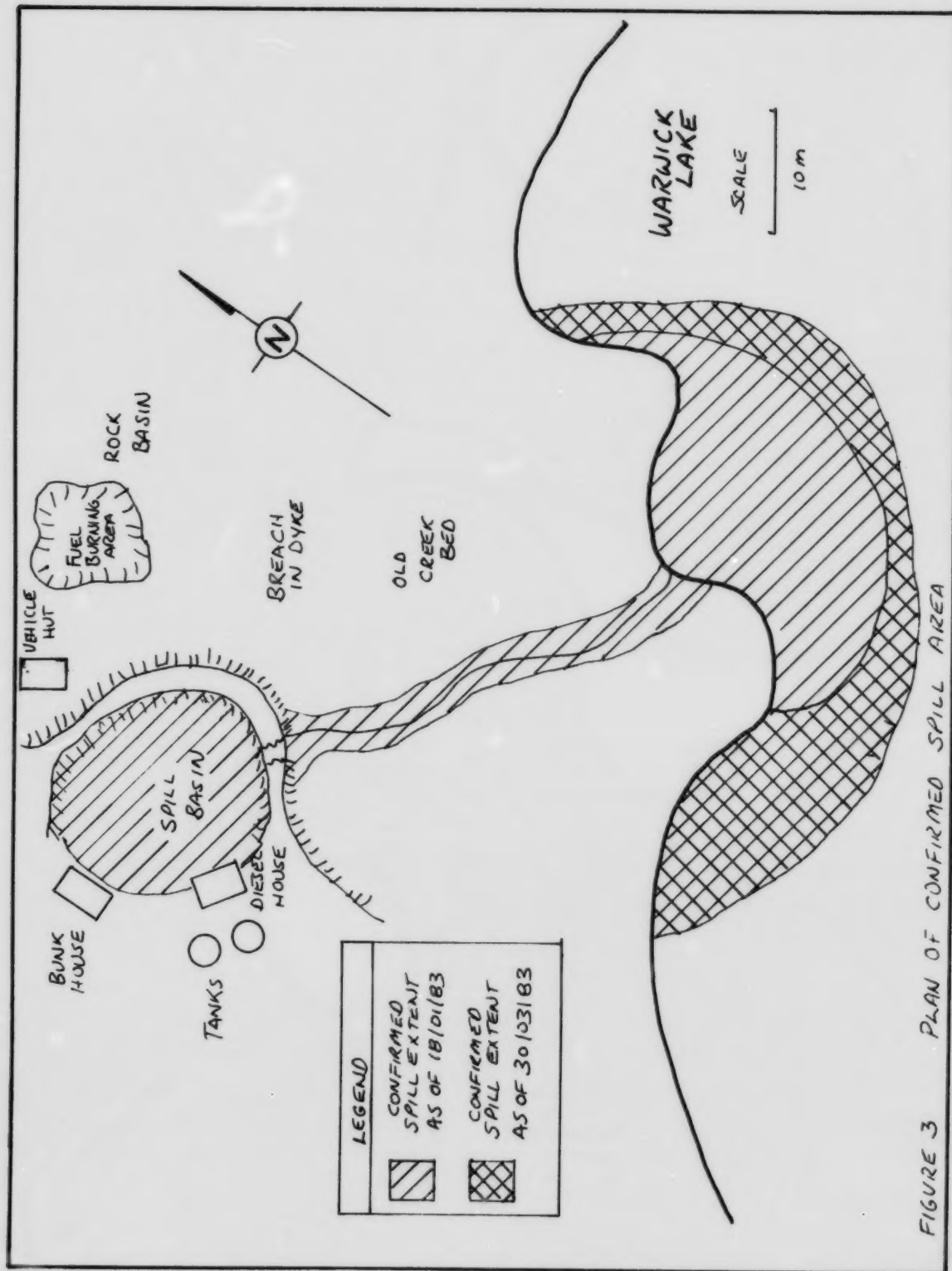
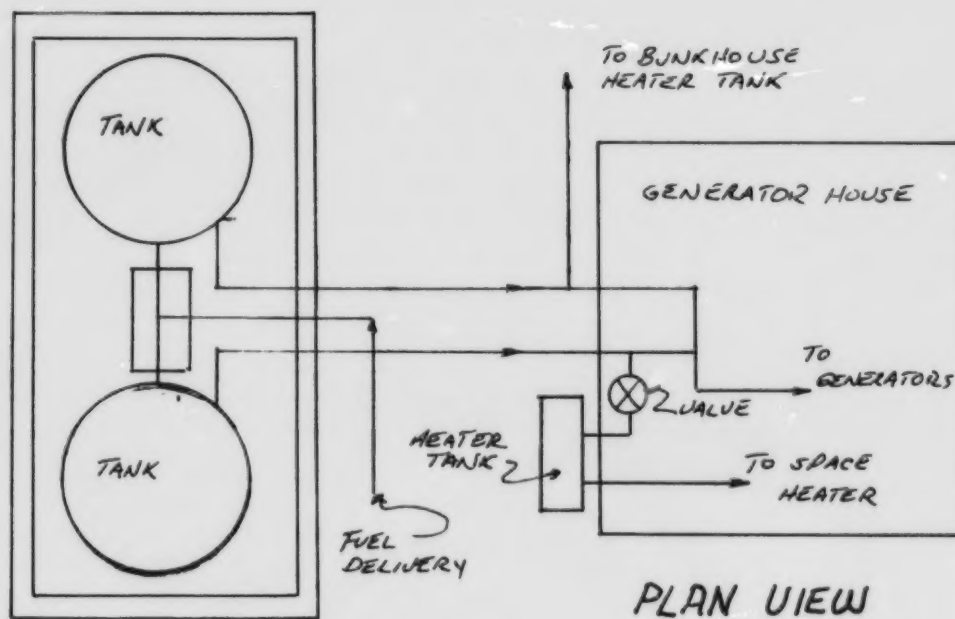
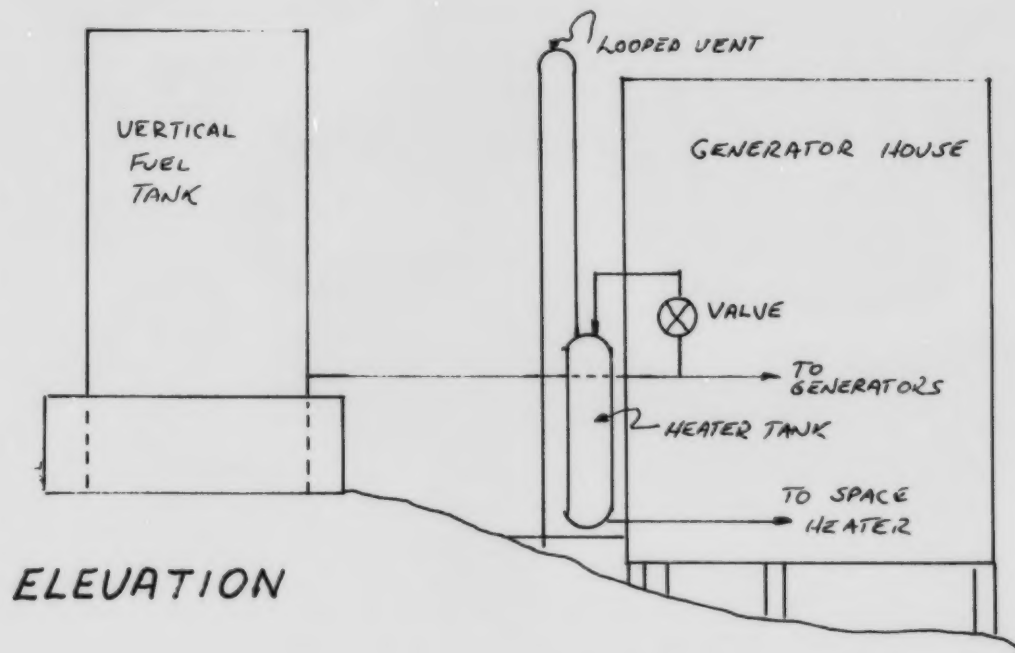


FIGURE 3 PLAN OF CONFIRMED SPILL AREA

FIGURE 4 TANK AND GENERATOR BUILDING SCHEMATICS



Plan of Attack

Once the extent of the spill had been determined a cleanup plan was formulated by the MOE officers and Bell Canada representatives. The spill could be broken down into three areas of concern; the spill catch basin; the old creek bed and; the lake surface.

The top priority for initial cleanup was the lake. Contaminated snow from the ice surface was to be scraped up and removed to a secure rock basin north of the diesel house. Contaminated snow thus collected could be burned to dispose of spilled product. This would also allow a closer examination of the ice surface to determine the actual extent of the fuel spread. Because limited cleanup equipment was available, all of the work would have to be done by hand, shovelling snow up into small trailer equipped snowmobiles, then transporting it to the rock basin for burning. It was also felt at that time that a boom would have to be sunk into the ice to contain any fuel not recovered prior to ice breakup.

Similar to the ice surface, contaminated snow from the creek bed would have to be shovelled up and burned in the rock basin. This would be the second area of priority. Any delay in removing the contaminated snow from this area would allow the fuel to thaw the ground frost and seep into the soil.

Since the containment dyke appeared to be capable of holding the fuel it had trapped, this was the final cleanup priority. The collapsed portion of the dyke would have to be temporarily repaired with fabric and sandbags. This would be necessary to ensure that trapped fuel remained trapped if a thaw raised the liquid level in the basin or if another spill occurred. Fuel and contaminated snow would also be removed to the rock basin for burning once the other areas had been cleaned up.

Several samples of contaminated snow were collected. These were collected as possible evidence for prosecution and to determine the fuel content of the snow. After the snow had melted the samples contained 5%-50% fuel by volume depending on the location.

Representatives from Bell Canada and their contractor, John Dugas, from Red Lake, indicated that cleanup crews could be on site and working within two days. It would take some time to get the required equipment into the site depending on the availability of cargo-aircraft.

The first cleanup crews arrived at the site and began work on January 20, 1983.

Clean Up Measures

On January 25, 1983 one of the MOE officers returned to the site along with an MNR fish and wildlife biologist. Contaminated snow was being burned on their arrival and could be observed from the aircraft.

By this time cleanup crews had scraped up contaminated snow from about 30% of the affected ice surface and had cleaned off about 10 m of the creek bed. The temporary repairs of the dyke had also been completed.

On January 24 the crew had cut a hole in the ice close to the shore and discovered that the fuel had flowed under the ice as well as on top of the ice. The 50 cm x 50 cm hole contained diesel fuel to a depth of about 30 cm. Crews had used a hand pump to pump fuel from the hole to 200 litre drums. A sample of this fuel, allowed to stand for about 1 hour, showed it

to be about 99% diesel fuel, since only a small quantity of water had settled to the bottom.

Because the fuel was now confirmed to be in the lake itself, the spill was more serious than first thought. A more intensive cleanup strategy was now required. Ice thickness was measured at a number of places and it was discovered that the ice became thicker as distance from shore increased. It is believed that this was partly a function of fuel contact with the underside of the ice as well as from the force of gravity tilting the ice from the centre to the shore.

It was decided that a series of 2 cm auger holes would be cut into the ice to determine the extent of under ice contamination. Once this was known a series of trenches would be cut into the ice leading to a collection reservoir. Because the fuel would float on the water surface this would allow the fuel to be pumped from the surface of the trenches. The fuel would also act as antifreeze preventing the trenches from freezing over. In addition a perimeter trench would be cut to prevent any fuel from migrating further out into the lake.

Burning of contaminated snow was well underway by this time. The first contaminated snow had been burned on January 21 and the cleanup crew was becoming very proficient in getting the fuel to burn. The procedure for burning was as follows:

- a) about 15-20 snowmobile trailer loads of contaminated snow were piled into the rock basin.
- b) a "tiger torch" was used to melt a small puddle of water at one corner of the snow pile.
- c) if the snow hadn't started to burn by this time a small quantity of raw fuel was poured onto the water puddle and ignited.
- d) once the fuel on the puddle began to burn, the reaction became self sustaining. The heat of the fire caused the snow to melt releasing the absorbed fuel. This fuel floated on the surface of the water and was consumed in the fire.

This process would continue with the intensity of the fire reaching a peak, then dropping off as less and less fuel was released until all of the fuel was burned off. This process would take approximately two hours. After several of these burns, the basin would fill up with melt water although some did evaporate.

Because this water contained residues of the fuel burn, crews were reluctant to pump this water from the basin. A 200 litre drum of fuel collected from the lake was poured into the basin and ignited. This fire burned very quickly and intensely. Flames reached 20-25 metres into the air and the fuel was consumed in about 4 minutes. Most of the residual water in the basin had evaporated. Following this experiment, crews would burn a drum of fuel after several snow burns to remove trapped water.

Because of the availability of the Bell Canada Bunkhouse, cleanup crews began working on a 5 day in 2 day out work schedule. The size of the work crew was limited to 3 or 4 because of the size of the accommodations and the amount of cleanup equipment. The cleanup continued at a slow but steady pace over the next few weeks.

By February 4, 1983 about 75% of the contaminated snow on the ice surface had been removed and burned. A 4,500 litre storage tank had also been flown into the site to store fuel pumped up from under the ice. A

series of large metal pans were fabricated on the ice to burn collected fuel, but were not used due to the danger of further contamination of the lake.

By February 25, 1983 most of the contaminated snow had been removed from the ice surface and had been burned. Efforts to pump fuel from beneath the ice had been stepped up. Crews found that the recovery of fuel from the collection trenches was increased when water was pumped on to the ice surface outside of the spill area. It is presumed that increased gravitational pressures exerted by the water created a slight tilt to the ice forcing more of the trapped fuel up into the trenches. It was estimated that by this time about 27,000 litres of the lost fuel had been recovered and burned. Approximately 2700 litres of that estimate had been recovered directly from the lake.

On March 10, 1983 the site was again visited by representatives of the MOE as well as an inspector from the Ministry of Consumer and Commercial Relations (MCCR) Fuel Safety Branch. By this time a series of collection trenches had been cut in the ice up to about 30 m offshore. Most of the ice surface and creek bed had been scraped and cleaned. Burning of contaminated snow was continuing. Because fuel had seeped into the ground on the creek bed the area was being burned with the assistance of wood and sawdust. The sawdust absorbed fuel from the soil and the firewood provided the heat necessary to sustain the burn. Black smoke emitted by the fire indicated the combustion of diesel fuel.

It was estimated that by this time about 37,200 litres or 60% of the original spill volume had been recovered. It was also estimated that the dyke contained up to 9,000 litres of fuel.

By March 30, 1983, 74 days after the initial discovery of the spill, the cleanup was essentially complete. All of the contaminated snow from the ice surface and the creek bed had been removed and burned. About 3,600 litres of fuel had been pumped from beneath the ice surface. About 9,000 litres of fuel was recovered from the dyke. During the cleanup of the dyked area a second ice layer was discovered below the level of the fuel. After the fuel was removed straw was placed on the ice to absorb fuel from the saturated ice. The straw was turned, removed and burned on a daily basis.

Approximately 260 m of boom was constructed onsite of lengths of construction lumber and plywood, linked together by heavy cable. This boom was sunk into the ice and anchored to the shore in such a fashion that any remaining fuel would be trapped behind the boom. In an effort to relieve pressure on the boom from ice break-up forces, the ice surface was scored with a chainsaw.

No further cleanup work could be done until after ice breakup with the exception of a visit to the site, by helicopter, on April 27, 1983. By this time the snow melt had been completed but the ice surface was still intact. Because the ice was "candling" (many pores and cracks) small pockets of fuel were visible on the ice surface. The cleanup crews ignited these pools of fuel successfully. Straw which had been placed on the old creek bed was inspected and found to be free of any residual fuel. The floating boom was still intact.

Assessment of Impact of the Spill

On June 2, 1983 the final MOE inspection of the cleanup was conducted. The floating boom had survived the stresses of ice-breakup. On inspection of the boom, a slight surface discoloration was noted but this was not considered significant and could be compared to that from an outboard motor.

The shoreline of the lake showed no indication of any fuel contamination and no environmental damage was noted other than the dead vegetation along the old creek bed. The creek bed area was slightly fuel contaminated but the contamination did not penetrate the soil for more than 2-4 cm. It was not expected that this would further contaminate the lake.

The containment dyke still held some of the spilled fuel and needed to be cleaned out. The surface of the clay material was contaminated with fuel and fuel was floating on the ponded water.

The rock basin where contaminated snow and fuel was burned was surprisingly free of evidence of the fuel burned there. Rocks were scorched and some burn residue (soot) was noted but no other evidence was present.

The cleanup was virtually complete as of the inspection of June 2, 1983. Some minor aesthetic cleanup work still remained, however, the cleanup efforts were considered successful in mitigating the hazards and damage to the environment. It is estimated that 50,000 litres of the lost fuel were recovered which represents about 85% of the estimated fuel loss. This estimate may be low since so little evidence of the fuel spill remained after cleanup. The estimated cost of the cleanup was \$200,000.00 not including the cost of fuel replacement.

Follow Up Measures

Following two smaller spills at similar remote fuel storage facilities the Ministry of the Environment made an inspection tour of 23 of these facilities across Northwestern Ontario in August of 1983. The purpose of the tour was to determine the fuel spill protection in place at the facilities and what environmental hazards the sites posed. The report of this inspection concluded that the level of spill protection was not adequate to prevent potential spills from causing considerable environmental damage.

As a result of this report, a working group made up of the Ministry of the Environment, Ministry of Consumer and Commercial Relations (Regulatory agencies), Bell Canada, Ontario Hydro, the Ministry of Transportation and Communications and the Ministry of Government Services (owner/operators of the sites) was formed to develop a plan to upgrade spill protection at these facilities.

The first step in the process was to identify all of the sites located in Northwestern Ontario. A total of twenty seven (27) sites were identified. In early 1984 a further "nuts and bolts" inspection tour was conducted. From this tour a list of priority sites was identified where upgrading of spill protection was immediately required. Once the priority sites were upgraded, other sites would have work done as required.

As of the end of 1987 all priority sites have been upgraded and work on other sites is continuing. As well all sites now have a spill contingency plan.

Monitoring programs for each site have been developed and include such

things as inspection of dyke integrity, removal of trapped storm water from dykes, inspection of fuel transfer pipes and condition of fuel storage tanks.

Although all fuel spills can't be prevented, spill protection works, contingency plans and a routine monitoring program are essential proactive measures necessary to reduce or eliminate the damage to the environment that results from spills of petroleum products. The cost of these items is only a fraction of the cost of the cleanup of a spill not only in dollars but in damage to the environment. The old adage "an ounce of prevention is worth a pound of cure" is nowhere as relevant as in fuel spills.

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The 1987 Newfoundland Oil Spill Experiment

An Overview

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Abstract

A joint Canadian-United States exercise involving the intentional spilling of approximately 20,000 gallons of specially-treated crude oil was conducted off Newfoundland in September 1987 to evaluate the containment and recovery capabilities of three state-of-the-art booms and skimmers. As part of the exercise, data were collected on a specially-instrumented oil spill boom in an attempt to verify a proposed performance test procedure for open-ocean oil spill booms. A visco-elastic chemical additive was used, after the equipment evaluation was completed to enhance recovery operations. Additional observations were made on the persistence of spilled oil slicks in advanced sea states. The containment and recovery effort was one of the most successful on record and was conducted in winds and sea states commonly thought to be beyond existing capabilities.

Introduction

An intentional oil spill of 18,000 U.S. gallons was conducted on September 24, 1987, offshore of St. John's Newfoundland to evaluate the containment and recovery capability of three booms and skimmers. The spill also provided an opportunity to verify a nonpolluting performance evaluation procedure for offshore oil containment booms. The spill was conducted approximately 25 nautical miles east of St. John's. Ocean dumping permit requirements included SSW currents and westerly winds to minimize chance of shoreline contact; water depths of at least 100 meters; the site had to be at least 25 nautical miles from shore, and the area had to be within 2 to 3 hours steaming from St. John's. The center of the area selected was 47 degrees, 40 minutes North and 52 degrees, 03 minutes West.

A crude similar to the typical high wax Grand Banks crude was unavailable. Brent crude from the North Sea was allegedly treated by adding 1 percent slack wax by volume to yield an oil of similar physical properties to the Grand Banks crudes. The modified oil was to have a density of 839.8 kg/m³ and a viscosity of 20 m Pas at 12 degrees C (Ross, 1987a). Recent information indicates that insufficient slack wax was added to reach the 1 percent by volume target level.

Meteorological conditions were recorded on the Canadian Coast Guard (COG) Cutter "Grenfell" at 15 minute intervals. These include corrected wind velocities and air and water temperatures.

A wave rider was deployed at the test site but failed to function during the exercise. Consequently, sea conditions were estimated, with reasonable agreement, by various trained observers.

The test plan called for the deployment of three booms as follows: A 250 meter length of the specially instrumented Oil and Hazardous Material Simulated Environmental Test Tank (OHMSETT) boom would be deployed in normal catenary. Approximately 20,000 gallons of treated Brent Crude would be spilled by the command/recovery ship Terra Nova Sea into the catenary. The oil would be held in the boom for approximately 1 hour while freeboard and draft data and visual observations of oil retention were recorded. During this period, 200 meters of the Canadian Coast Guard's RO-BOOM would be deployed behind the OHMSETT boom. The tow speed would be increased to significant loss speed (0.5-1.0 knot). One end of the boom would then be released and the oil discharged into the RO-BOOM. Oil would be held in the RO-BOOM for approximately 1 hour while the oil retention capabilities were observed. The St. John's Coast Guard Vikoma Ocean Pack boom (400 meters) would be deployed behind the RO-BOOM during the observation period. The last procedure involving lost tow speeds would be repeated with the RO-BOOM, and the oil would be released into the Vikoma.

Oil would be retained in the Vikoma for approximately 1 hour. The Terra Nova Sea would then commence skimmer evaluations. Two skimmers, the Framo ACW400, and an innovative Coast Guard Heavy Oil Skimmer (HOS) would be evaluated for 20 minutes each and the remaining contained oil would be recovered by the skimmer with the better performance (Ross, 1987b).

The intent of the OHMSETT boom deployment would be to verify the hypothesis that a boom's ability to contain oil is correlated with its ability to sea keep or comply with wave-induced surface motion. If this hypothesis could be verified and quantified, future performance evaluations of offshore containment booms could be restricted to measuring seakeeping capabilities in a range of sea states. No further spills of the 20,000 gallon size of light and heavy oils would be required, in a range sea states, to evaluate each type of boom. Ocean dumping permits are difficult to obtain and intentional oil spill exercises of this magnitude approach the million dollar funding level. Intentional spills also constitute a risk of potential damage to the immediate environment. Clearly a cost-effective and nonpolluting evaluation procedure for offshore equipment is necessary to develop a predictive capability for the performance of offshore response equipment. Wind conditions desired were sea state 2 to 4, and winds from 10 to 20 knots.

Practice Run - September 21, 1987

The ships and smaller vessels sailed at 6:00 a.m. and proceeded to a location 5.5 miles off Torbay point. The CCG Grenfell then deployed the OHMSETT boom and passed one end to the CCG cutter 212 which took the boom in tow. The CCG cutter 206 then attempted to pick up the trailing end of the boom, a job which took 45 minutes. As soon as the 206 had the end of the boom secured, the two cutters attempted to tow the boom, in a "U" configuration, into a position astern of the Terra

Nova Sea. This resulted in the OHMSETT boom immediately beginning to twist on itself, and 1 hour was lost in straightening the boom. Eventually the boom was positioned relative to the Terra Nova Sea and simulated discharge of the oil was carried out. Data collection, without oil, for almost 1 hour followed.

While the OHMSETT boom was being deployed and positioned, the RO-BOOM was deployed from the CCG Sir Humphrey Gilbert and passed to CCG cutter 214. This procedure took almost 2 hours and, the RO-BOOM was rapidly positioned with respect to the OHMSETT boom because both the Cutter 214 and a Boston Whaler were able to tow the boom at speeds of 5 knots. With the RO-BOOM in position, the CCG cutters 212 and 206 commenced to maneuver, presumably to form a "J." The CCG cutter 206 then snagged the OHMSETT cable in her screws and cut it, disabling herself. This resulted in delay in the exercise while the cable was freed and, because CCG cutter 214 and the Boston Whaler were now approaching closely, the Cutter 212 took the boom and Cutter 206 in tow and cleared the area so as not to impede the exercise.

During the period in which the RO-BOOM was being deployed, the CCG Grenfell deployed the Vikoma boom. Once the simulated oil release was over, the Terra Nova Sea took the other end of the boom and the vessels formed a Catenary. After holding position relative to the RO-BOOM for a period, the ships formed a "J" with the boom and practiced deploying the skimmers.

All ships returned to harbour by 5:00 p.m.

Period Between the Dry Run and the Trial

Several meetings of the senior people involved in the exercise occurred between September 21 and September 23, 1987. It was decided to remove CCG cutter 206 from the exercise. The Boston Whaler was able to tow and hold the boom in sea state 1, but it was recognized that this would be difficult, with oil, in the desired weather. The Newfoundland Fisheries department had provided a vessel, the Bernier, and it was decided to use her and a second chartered OSV to tow the RO-BOOM.

Concern was registered that the weather might, surprisingly, be too calm on September 24, the day which looked best for the actual trial. It was, therefore, decided to interchange the OHMSETT and RO-BOOMS to take advantage of the higher winds and waves expected later in the day.

The long time required to deploy the RO-BOOM from the Sir Humphrey Gilbert led to the decision to deploy that boom from the second OSV, the Triumph Sea. Repairs were carried out on the OHMSETT boom cabling and the boom with instrumentation, was functional by 5:00 p.m. on September 23.

Since the Terra Nova Sea had oil recovery tanks on board, it was decided to dispense with the dumb barge and to release the oil directly from that OSV.

Trial with Oil on September 24, 1987

The Triumph Sea and the Bernier sailed at 3:00 a.m. All other vessels sailed at 4:00 a.m., and everyone was on station by 6:45 a.m. The Triumph Sea commenced deployment of the RO-BOOM enroute and by 7:30 a.m., the boom was ready to receive oil. Once the OHMSETT boom was deployed, at 8:15 a.m., the oil was pumped into the RO BOOM with supervision from the helicopter and a small boat.

All oil was in the boom by 9:00 a.m.

It was decided to give the news media a chance to view the test from the air and this was done from 9:00 a.m. to 10:00 a.m. During this period, the CCG cutters 212 and 214 attempted to pull the OHMSETT boom into proper position astern of the RO-BOOM and keep it there. Every attempt to move the boom, in a catenary, in the 15 knot winds blowing at the time resulted in the boom twisting. As a result the OHMSETT boom fell progressively further astern of the RO-BOOM.

At 10:30 a.m. the oil in the end of the pocket of the RO-BOOM was 30 cm thick, the wind was 15 knots, and some splash-over and significant drainage under the boom were occurring. The vessels, therefore, formed a "J" and released one end of the boom to allow the oil to flow into the OHMSETT boom. The OHMSETT boom was approximately 1 km astern, and the vessels were having trouble towing the boom in a catenary without the boom twisting. It was, therefore, decided to direct the cutters with the OHMSETT boom, to the oil, by helicopter, keeping the boom in a straight tow. After 20 minutes, the cutters were adjacent to the thick oil, and, after a further 20 minutes approximately 80 percent of the thick oil was in the OHMSETT boom. The remaining 20 percent was contained in the Vikoma boom. Data collection on the OHMSETT boom started as soon as the oil was captured and continued for 56 minutes. The CCG cutters then stopped across the path of the vessels towing the Vikoma boom and released one end of the boom. The oil spilled into the Vikoma boom catenary, and one CCG cutter trailed the OHMSETT boom at the throat of the catenary allowing the waves to wash the oil into the Vikoma boom.

The CCG Grenfell and Terra Nova Sea towed the oil filled Vikoma boom for approximately 1 hour. During this time, the wind had freshened to 15 knots to 20 knots. The boom was moving at over 1.1 knots relative to the sea, and some oil was being lost (approximately 3 mm thick). The CCG Grenfell then attempted to move ahead to form the "J" for the skimmers. Not being very maneuverable, she quickly reached 3.4 knots and the oil was lost.

With the oil now lost, the weather abated slightly. The RO boom was still streaming astern of the Triumph Sea so it was decided that she and the Bernier would form the boom into a catenary and attempt to recover the oil downwind. The helicopter had been lost to the exercise for approximately 1 hour at this time. As soon as it returned, it was refueled and sent up to assist. In the interim a small boat was used to guide the tow vessels into the heaviest portions of the slick. When the helicopter was over the thick oil, it was apparent that the vessels with the RO-BOOM were adjacent to some of the oil and unable to see it. They were, therefore, directed

from the air and small boat, and managed to collect 80 to 90 percent of the thick oil which was on the surface at the time.

Oil was successfully contained and recovery was attempted using the three skimmers on board the recovery-command vessel. The first skimmer, the Heavy Oil Skimmer (HOS), was deployed and no measurable recovery was observed. The oil used was modified by adding petroleum wax so that it would resemble a typical Grand Banks crude oil. This type of oil is uncharacteristic of most crudes in that it possesses low adhesive properties. Therefore, oleophilic skimmers, which depend upon the adhesive nature of the recovered oil, do not perform well with high parafin-based oils. This was again proven with the oleophilic HOS skimmer. The skimmer was recovered after several trained observers were satisfied that the HOS skimmer had had sufficient evaluation time in the contained slick. Problems with the ability of the support arms, used to suspend both the HOS and Framo skimmers, to adjust to the roll of the vessel and short period wave action resulted in both skimmers being frequently submerged so that oil and water were washed into the sump of the skimmer.

The second skimmer the "Framo ACW-400" was deployed. The overall rate of oil recovery of the Framo was 60 gallons per minute with unknown amounts of the recovery resulting from frequent partial submergence.

At this point, it was decided by the On-scene Commander that the skimmer evaluation was complete. Additional measures were needed to ensure recovery of the remaining contained oil because the weather was deteriorating and night was falling. Accordingly, approximately 7 pounds of the visco-elastic agent "Elastol" were spread from an 8-ounce styrofoam coffee cup into the estimated 7,400 gallons of oil and oil water emulsion in the containment boom. Elastol was added because previous research funded by the Minerals Management Service and Environment Canada had shown that the elastic and adhesive properties of the oil could be increased by addition of the agent, thus making the oil more readily capturable with these types of skimmers. The Framo ACW-400 was retrieved from the slick as the "Elastol" was added and because of the operational constraints on the recovery operation, due to the weather and lateness of the day, the skimmer was not redeployed.

The weir-type skimmer, Pharos Marine GT-185, was deployed into the treated slick and recovered near capacity rates of 85 gallons per minute of oil and oil emulsion with no free water. This recovery rate was higher than anticipated and may have been even higher if the oil had been untreated. Treatment significantly increased the viscosity of the oil. The skimmer was removed from the slick, cleaned, and stored on board.

The HOS skimmer was redeployed and failed to function because of a piece of steel in the return pump. The skimmer was recovered, the steel piece removed, and then the skimmer was redeployed.

The HOS skimmer yielded a recovery rate of 50 gallons per minute with a portion of the oleophilic fabric on one of its two drums damaged. Debris was collected at this time in the ventury system used to measure recovery fluid flow rates. The debris may have contributed to the subsequent failure of the HOS skimmer return hose. No flow-rate measurements were taken before the failure. Visual observations on the amount of oil adhering to the oleophilic fabric of the HOS skimmer indicated that recovery rates were significantly increased by the addition of "Elastol."

Operations were suspended because of the advancing sea states and increasing darkness.

An overflight of the area, by helicopter, was carried out during the skimming operation. This revealed a sheen approximately 2.5 by 0.5 nautical miles with 3 patches of brown oil. It is estimated that no more than 260 gallons of oil remained in the thick patches. A further flight 18 hours later showed that only small brown patches and sheen remained, and this was rapidly dispersing.

Lessons Learned or Relearned

- o Thorough proficiency with the recovery equipment to be used is essential.
- Routine practice is required.
- o Large volumes of oil are necessary to realistically evaluate performance of offshore response equipment.
 - o The use of helicopters to direct the placement of tow vessels and the use of small vessels to monitor and advise on boom conditions are essential to maximize the efficiency of conventional recovery operations.
 - o Accurate measurements of the meteorological and sea conditions are necessary for accurate analysis of the evaluations.
 - o The requirements for slow-speed towing and maneuvering of large containment booms necessitate the use of vessels with variable pitched propellers, thrusters, and good seamen in control.
 - o It was not possible to form a recovery configuration with two vessels while towing upwind. The third vessel was necessary for recovery in normal catenary.
 - o The upper meteorological and sea state limits for downwind containment and recovery were not reached during this test.
 - o Upwind collection proved impossible when winds approached 15 knots. This is consistent with many past observations for containment operations conducted upwind.
 - o Steps should be taken to avoid loss of contained oil by shipboard discharges such as cooling water impinging upon the slick.
 - o Tankage should be available for recovery of several times as much fluid as discharged to account for the oil and water emulsions and free water recovered.
 - o Analysis of the correlation of the ability of a boom to seakeep with its ability to contain oil is continuing.

- o Recovery of high wax oils similar to Newfoundland crudes in 10 degrees C water is significantly enhanced by the use of "Elastol."

Disclaimer

Mention of specific products in this paper does not constitute or infer endorsement or acceptance by the Minerals Management Service, the Conservation and Protection, or the authors.

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OFFSHORE TESTING OF BOOMS AND SKIMMERS

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INTRODUCTION

These offshore trials of oil spill containment and recovery equipment came about in order to meet several needs identified by various agencies. Foremost was the desire to find out whether or not offshore containment and recovery equipment presently stockpiled by the Canadian Coast Guard was suitable for use on spills of oils typical of the waxy crude oils discovered on the Grand Banks. These oils exhibit atypical spill behaviour (S.L. Ross and DMER 1987) and may not be amenable to recovery with conventional oleophilic or weir-type skimmers (S.L. Ross and Hatfield 1986). As well, the operating characteristics of the RO-BOOM and Vikoma Ocean Pack boom were to be compared to determine whether or not one best suited the needs of Coast Guard. In addition there was a desire to field test a novel skimmer developed for the Coast Guard for heavy, viscous oils (Canpolar 1986) on waxy crude oil. Coincidentally, the Oil and Hazardous Materials Environmental Test Tank (OHMSETT) Interagency Technical Committee (OITC) had a need to verify at sea, with oil, a boom testing protocol intended to correlate a boom's ability to contain oil with its seakeeping ability. If successful this protocol would preclude the need for most offshore testing of booms with oil. Trials with a specially instrumented boom had been conducted in the OHMSETT tank with oil and offshore without oil; these trials were to be the final component of the test program: tests offshore with and without oil.

Objectives

The objectives of the offshore trials were to document and quantify:

- * the sea-keeping and waxy oil containment capabilities of the Vikoma Ocean Pack and RO-BOOM in seas representative of Grand Banks conditions;
- * the waxy oil recovery capabilities of the Framo ACW-400 type skimmer and the experimental Heavy Oil Skimmer; and
- * the sea-keeping and oil retention capabilities of a specially instrumented offshore oil boom in seas representative of offshore conditions.

This paper documents the methodology, results, conclusions and recommendations arising from the study pertaining to the first two objectives noted above. A separate paper is being written on the final objective of the study by OHMSETT staff (McKowan and Borst 1987).

Test Site Selection

The proposed test area was selected in consultation with the Regional Ocean Dumping Advisory Committee (RODAC) based on the following criteria:

- * any minor oil losses must drift out to sea (SSW currents and westerly winds)
- * at least 100 m water depth

- * at least 20 nm offshore
- * within 2 to 3 hours sailing from St. John's

The site chosen was an area (Figure 1) centred at 47° 40'N, 52° 03'W east of St. John's. An area, rather than a specific site was selected to permit flexibility in test selection on the day of the trials and to account for "over the ground" drift during the trials.

The site and the possible time window for the trials (September 1 to October 31, 1987) were specifically chosen to avoid conducting the trials during the fishing season and to optimize the chances of suitable sea and weather conditions.

EQUIPMENT AND METHODS

The Oil

Due to the unavailability of sufficient quantities of a Grand Banks crude (about 75 m³ was required as the volume necessary to provide realistic contained slick area and thickness) it was necessary to produce an oil with properties similar to those typical of Grand Banks' crudes (Table 1).

TABLE 1
COMPARISON OF OIL PROPERTIES

OIL —	API GRAVITY —	DENSITY @ 15°C (KG/M ³)	VISCOSITY (mPas)	POUR POINT (°C)
HIBERNIA	36	844	11 @ 15°C	6
AVALON	29	877	93 @ 15°C	10
TERRA NOVA				
DST-1	31	871	8.7 @ 50°C	27
DST-2	32.9	861	16.7 @ 25°C	12

In order to achieve this, Brent crude, from the North Sea, was modified by the addition of 1% by volume of slack wax (the unprocessed wax precipitate from crude oil refining operations) to raise its pour point from 0° to 6°C. Laboratory weathering studies showed that the pour point of this oil as a 10 cm thick slick in a 9 m/s wind at 15°C would increase from 6°C to 15°C in ten hours. Since there was a desire to test the OHMSETT instrumented boom (scheduled to be tested first) with a fluid oil, this degree of pour point elevation was judged to be optimum for the expected 10–12°C waters.

The fresh, doped Brent crude had a density of 839.8 kg/m³ and a viscosity of 20 mPas at 12°C.



FIGURE 1 - LOCATION OF SUGGESTED TEST AREA

Environmental Data Gathering

Meteorological Information Wind speed and direction were recorded every 15 minutes during the trials using the anemometer and weathervane mounted on the CCGS Grenfell. These readings were subsequently corrected for the vessel's speed and heading. Water and air temperatures were also determined periodically throughout the day with mercury-in-glass thermometers.

Sea State Although a waverider buoy was deployed at the test site, and had functioned perfectly during the dry run two days previously, no detailed wave data were collected due to receiver failure. Visual estimates of wave height, length and period and swell height, length and period were made intermittently throughout the trial.

Boom Performance

Boom configuration was recorded by aerial and surface video and still photography. Relative boom/surface water velocity was measured by timing the drift of wood chips over a known distance along the side of the boom tow vessels. This data was converted to a relative velocity at the boom pocket by:

$$V = \frac{(U_1 + U_2)}{2} \cos (\theta/2)$$

where V = relative boom/water velocity (m/s)
 U_1, U_2 = measured drift at tow vessels 1 and 2 (m/s)
 θ = angular separation of the two vessels ($^\circ$)
 = difference in vessel headings at time of drift measurement

The rate of oil leakage from the booms was estimated from aerial video and still photography by determining the width of sheen leaking past the boom and multiplying by the relative boom/water velocity and an assumed slick thickness (10 μ m for sheen, 1 mm for dark oil). This technique provides a reasonable relative comparison of boom leakage rates for booms tested under similar conditions; more accurate quantitative data would be available if the aerial photography had been supplemented with surface slick thickness data. This was not deemed necessary by the project steering committee.

General boom performance (wave conformance, ease of deployment, and recovery, durability, manoeuvrability etc.) were monitored throughout the trial and recorded by surface video and still photography.

Skimmer Performance

The deployment, operation and retrieval of the three skimmers was recorded on videotape and still photographs. Observations on general skimmer performance (sea keeping, proximity to thick oil, flow of oil to skimmers, etc.) were made visually by trained personnel.

The recovery performance of each skimmer was measured by OHMSETT staff using the following equipment:

- * a 10 cm (4 inch) Venturi meter with Rosemount pressure gauges and a Telog data recorder was used to monitor fluid flowrates from each skimmer during recovery operations. The output used from the data recorder was a 3 second average flowrate. Twenty consecutive outputs were later averaged to give a one minute average flow. This was necessary to remove the effects of the vessel's roll on the pressures recorded;
- * periodic soundings of the 23 m³ (6000 gallon¹) receiving tanks were made to measure recovered fluid volumes;
- * small samples of recovered fluid were drawn from the skimmer discharge every five minutes during recovery operations and analyzed for density (by weighing a known volume), viscosity (Brookfield viscometer) and water content (by centrifugation followed by volumetric analysis);
- * stratified samples (covering 15 cm = 6 inches of fluid each) of the recovered fluid in the two tanks were taken with a Johnson sampler and analysed for oil, free water and emulsified water content to determine overall oil recovery factors.

3.0 RESULTS AND DISCUSSION

General

Figure 2 shows the sequence of activities on the day of the trials. Due to the need for sea state 3-4 related to the OHMSETT instrumented boom data collection and in view of the forecast wind and wave conditions it was necessary to alter the test protocol and release the oil into the RO-BOOM first, test the RO-BOOM and then release the oil into the OHMSETT instrumented boom.

The oil was pumped from the stern of the M/V Terra Nova Sea, commencing at 0846 and finishing at 0944, into the mouth of the RO-BOOM being held by the M/V Triumph Sea and the M/V Beinir (Figure 3). Some 67.7 m³ (17,885 gal) of oil were released in this manner at approximate position 47° 42'N, 52° 47'W. All the oil entered the mouth of the boom catenary.

From 0944 to 1050 the seakeeping and oil containment capabilities of the RO-BOOM were evaluated at relative boom/water velocities of less than 0.4 m/s 0.75 knots (Figure 4). The oil was released from the RO-BOOM by letting go the tow line from the M/V Beinir at 1050; no testing to first loss (i.e., towing at speeds in excess of 0.5 m/s = 1 knot) was conducted with the RO-BOOM.

Difficulties were encountered in holding the OHMSETT instrumented boom in position without the boom twisting. As such, at the time of the oil release from the RO-BOOM, the OHMSETT instrumented boom was approximately 1.5 km downdrift of the thick oil. After about an hour of manoeuvring, a portion of the thick slick was captured by the OHMSETT instrumented boom. During this time the Vikoma boom was deployed in a catenary in the path of the drifting thick oil (Figure 5). Testing of the OHMSETT instrumented boom commenced at 1210 and concluded at 1302.

1. in this report gallons refer to U.S. gallons (1 m³ = 264 U.S. gal)

FIGURE 2
TRIAL TIMETABLE

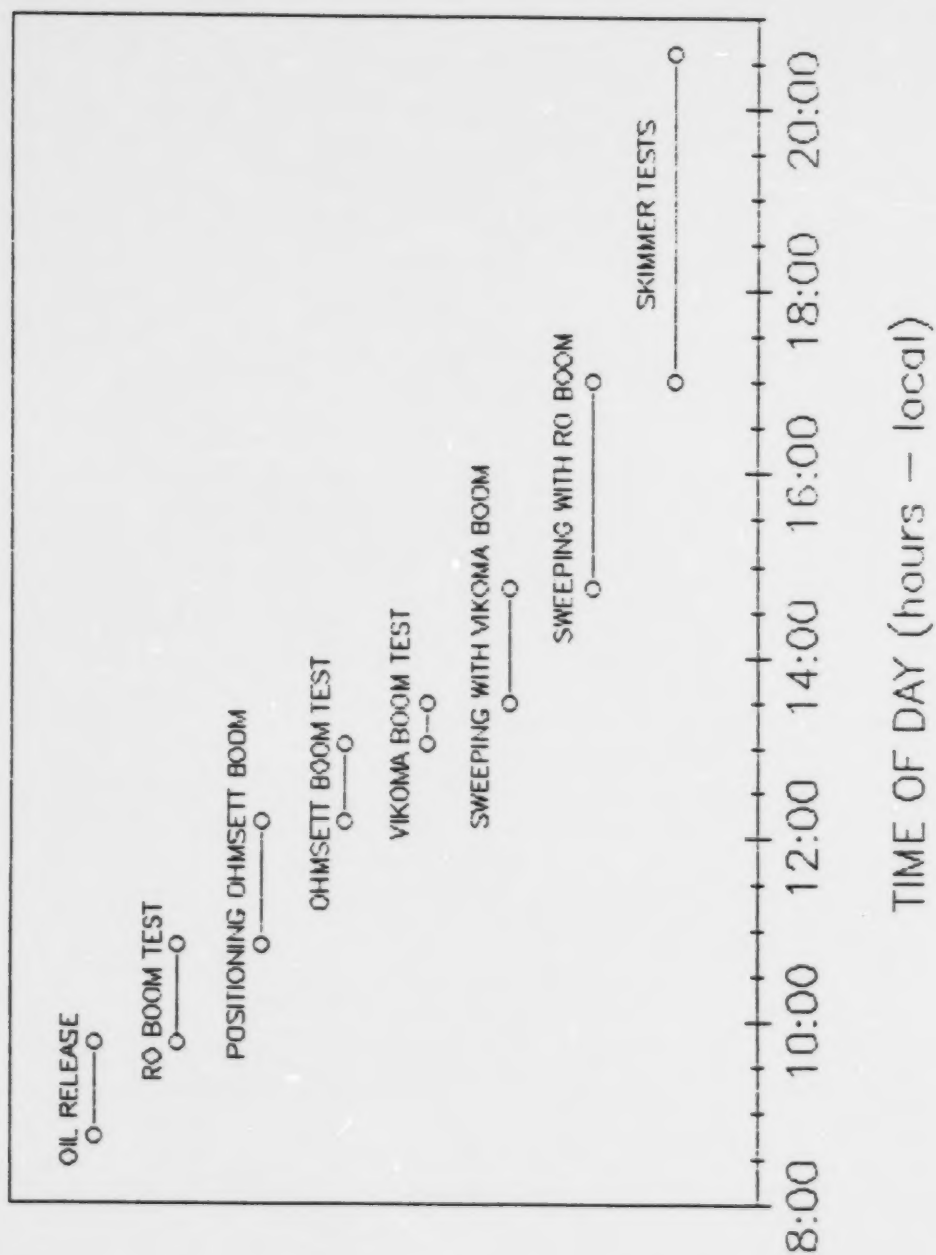




Figure 3 - Oil drifting into RO-BOOM



Figure 4 — Testing of RO-BOOM; note thick oil in pocket. Losses are seen only.



Figure 5 — Vikoma Ocean Pack deployed behind OHMSETT instrumented boom in path of slick

Although the Vikoma boom was positioned across the drift path of the slick, in manoeuvring to intercept the oil released from the OHMSETT instrumented boom at the completion of its test, some of the thick oil not originally contained by the OHMSETT boom drifted past the mouth of the Vikoma boom (Figure 6). This manoeuvring also caused the loss of the small volume of oil already collected. After one half hours testing of the Vikoma boom containing thick oil, the M/V Grenfell (on the starboard) began to slowly move ahead to form a "J" boom configuration for the skimming tests. Unfortunately, because the vessels were heading into a 7–10 m/s (15–19 knot) wind, the Grenfell moving forward caused the relative boom/water velocity to exceed 0.5 m/s (1 knot) and all the oil collected escaped by 1348 (Figure 7). Following this the Vikoma boom was repositioned with the vessels heading downwind and some thick oil was recaptured by the Vikoma boom. Much of this oil was lost under the boom a second time when manoeuvring to form a "J" boom configuration for the skimming tests due to excessive speed. Attempts were made to deploy the Heavy Oil Skimmer at 1445 into what remained of the oil in the Vikoma boom however the boom pocket had collapsed and it proved impossible to insert the skimmer into the oil.

Between 1500 and 1700 the RO-BOOM was used in a "U" configuration oriented downwind to chase down and capture the thick oil slicks. From 1700 to 2036 the skimmer tests were conducted from the skimmer vessel (M/V Terra Nova Sea) stationed broadside to the RO-BOOM pocket (Figure 8).

The skimmers were tested in the following sequence:

- 1) The Heavy Oil Skimmer was deployed; no recovery was observed.
- 2) The Framo ACW-400 skimmer was deployed and operated for 23 minutes. During the last few minutes of this test Elastol was applied to the contained oil.
- 3) The Heavy Oil Skimmer was deployed; problems with the pump precluded recovery operations and one drum was damaged.
- 4) The GT-185 skimmer was deployed and operated for 29 minutes.
- 5) The Heavy Oil Skimmer was redeployed with only one drum fully operational. During this last attempt the discharge hose burst just as the initial measurements of recovery were being made.

The trials ended at 2036 due to the failure of the Heavy Oil Skimmer, darkness and increasing winds forecast for the area.

Environmental Conditions

Winds The wind speed remained relatively constant in the morning at 5 to 6 m/s (10 to 12 knots) and increased in the afternoon to 7 to 9 m/s (14 to 18 knots). Winds in the evening increased further to 9 to 10 m/s (18 to 20 knots). The wind direction remained relative constant from the southwest. Over the following 48 hours the winds shifted from southwesterly to westerly and averaged 4 to 8 m/s (8 to 16 knots), increasing to 8 to 13 m/s (16 to 25 knots) with gusts to 18 m/s (35 knots), 48 hours after the completion of the trials.

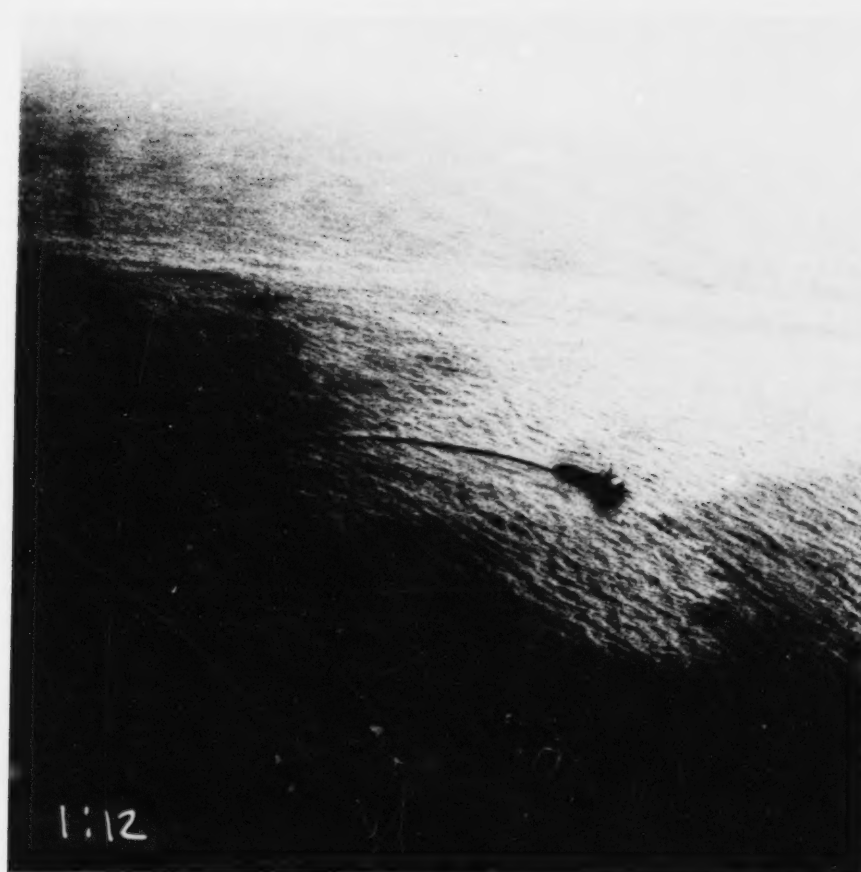


Figure 6 — Vikoma Ocean Pack being manoeuvred to intercept oil from OHMSETT instrumented boom.



Figure 7 — Oil lost from Vikoma Ocean Pack during manoeuvring boom into "J"

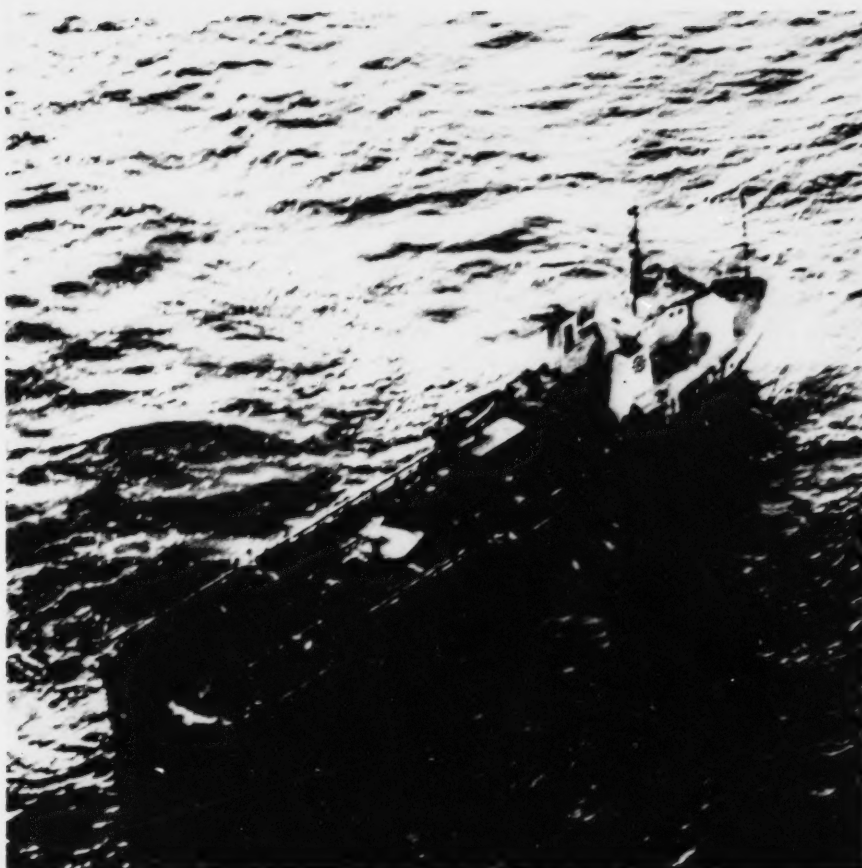


Figure 8 — Skimmer tests being conducted in pocket of RO-BOOM

Sea State At the commencement of the trials the waves averaged 0.5 m (Sea State 2) with a swell of 2.5 m (personnel in small boats reported occasional swells of 4 m). As the day progressed the wave height increased to about 1.3 m (Sea State 3-4) and the swell height decreased to 1.5 to 2.0 m.

Temperature The water temperature remained constant at 12°C throughout the day. Air temperatures increased from 12°C at sunrise to 14°C by sunset.

BOOM PERFORMANCE

This section of the report deals only with the evaluation of the RO-BOOM and Vikoma Ocean Pack. Details of the testing of the OHMSETT instrumented boom (McKowan and Borst 1987) are covered in a separate paper.

Deployment and Recovery

RO-BOOM The deployment of the two 200 m sections of the RO-BOOM required approximately 110 minutes over the gunwale of the CCGS Sir Humphrey Gilbert during the dry run and 105 minutes over the stern of the M/V Triumph Sea during the trials. Deployment over the stern of a supply boat was much easier than over a gunwale.

Recovery of the RO-BOOM over the gunwale took 80 minutes and was very difficult even in the calm conditions prevalent during the dry run. Up to 14 personnel were involved in boom recovery in this instance. Recovery over the stern of a supply boat was much less labour intensive (six personnel) and easier even though it was dark and the winds and seas were much higher than during the dry run. The time required to recover the boom was 100 minutes, slightly longer than during the dry run because the boom was rinsed of oil as it was being recovered.

Vikoma Ocean Pack The deployment of the Vikoma boom was accomplished in approximately 20 minutes during both the dry run and the trial. Recovery onto the hydraulic reel took about 30 minutes each time, however, it was necessary to remove the boom from the reel after each recovery and restow it into the boom box. This required about an hour. Deployment required three personnel; recovery required six, and restowing the boom required eight personnel.

Comparison The deployment and recovery of the Vikoma boom is faster and less labour intensive than that of the RO-BOOM, however, in the context of offshore spill response both booms were judged to be acceptable, providing these operations are conducted from the aft deck of a supply vessel. It should be noted that Roulunds, the manufacturers of the RO-BOOM, are continuing to improve the valving system and hope to reduce deployment times to about 10 minutes per 200 m section.

Manoeuvring and Durability

Both booms proved to be very manoeuvrable and no problems with overturning or twists were noted. No damage to the RO-BOOM was noted after 17 3/4 hrs

deployment including 3 hrs skimming operations; all the floatation chambers were still fully inflated when the boom was recovered.

The Vikoma boom suffered one incident of sinking when excessive strain during manoeuvring caused the band holding the air chamber to the power unit to slip off. This problem was rectified in about one half hour and the boom itself was undamaged.

Overall, the RO-BOOM was judged to be somewhat more durable for long-term offshore deployment because it does not depend on the continuous operation of a power source and the tearing and loss of one or more floatation units should not affect the overall integrity of the boom. Power failures and large tears can cause temporary losses of containment capability for the Vikoma Ocean Pack. Both booms were judged sufficiently manoeuvrable and durable for use offshore.

Sea Keeping and Oil Retention

RO-BOOM Oil was in contact with the RO-BOOM for two time periods during which data on seakeeping and oil retention was collected: first during the oil release and RO-BOOM trials from approximately 0900 to 1050 and second during the skimmer trials from 1700 to 1900 hrs. At all times the RO-BOOM followed the waves and swell very well and maintained its desired configuration.

Figure 9 compares the visually estimated oil leakage rate from the RO-BOOM during its morning trials with the calculated relative boom/water velocity. Also shown are the calculated wind-induced surface water velocity and measured (from aerial videotapes) slick drift rate. The three measures of relative water velocity agree reasonably well; the calculated relative boom/water velocity is generally slightly higher than the other two due to the need for the one tow vessel (M/V Beinir) to maintain steerage way.

The estimated relative oil leakage rates are very low initially at approximately 0.1^2 because only small amounts of oil had reached the boom pocket (Figure 10). By 0930 when most of the oil had reached the boom pocket the leak rate had increased to 0.5 to 1.0 (Figure 11); this leak rate remained reasonably constant throughout the test period (Figure 9). Some splashover of oil at the joints between floatation sections was observed near the end of the test (around 1050) when the winds had increased to 7 m/s (15 knots) and the relative boom/water velocity was calculated to be around 0.3 m/s (0.6 knots). The volumes of oil lost were not considerable.

One thickness measurement in the boom pocket near the end of the test period was reported; it indicated the contained slick to be an estimated 30 cm thick at the boom. Simultaneous aerial video and still photography shows an area of contained oil of some 200 m^2 . Assuming the slick thickness was relatively constant throughout (Wicks 1969; Lau and Kirchhefer 1974; Delvigne 1984), this would translate to a contained volume of approximately 60 m^3 or almost all the 67.7 m^3 discharged. No additional data was collected to confirm the variation in slick thickness, although the low observed leakage rates would tend to substantiate the conclusion that virtually all the oil released into the RO-BOOM was contained for the duration of its test and

-
2. the procedure used to arrive at this number results in units of L/s, however without actual slick thickness data to work with the numbers can only be used for relative comparison and are reported without units.

FIGURE 9
RO-BOOM LEAKAGE

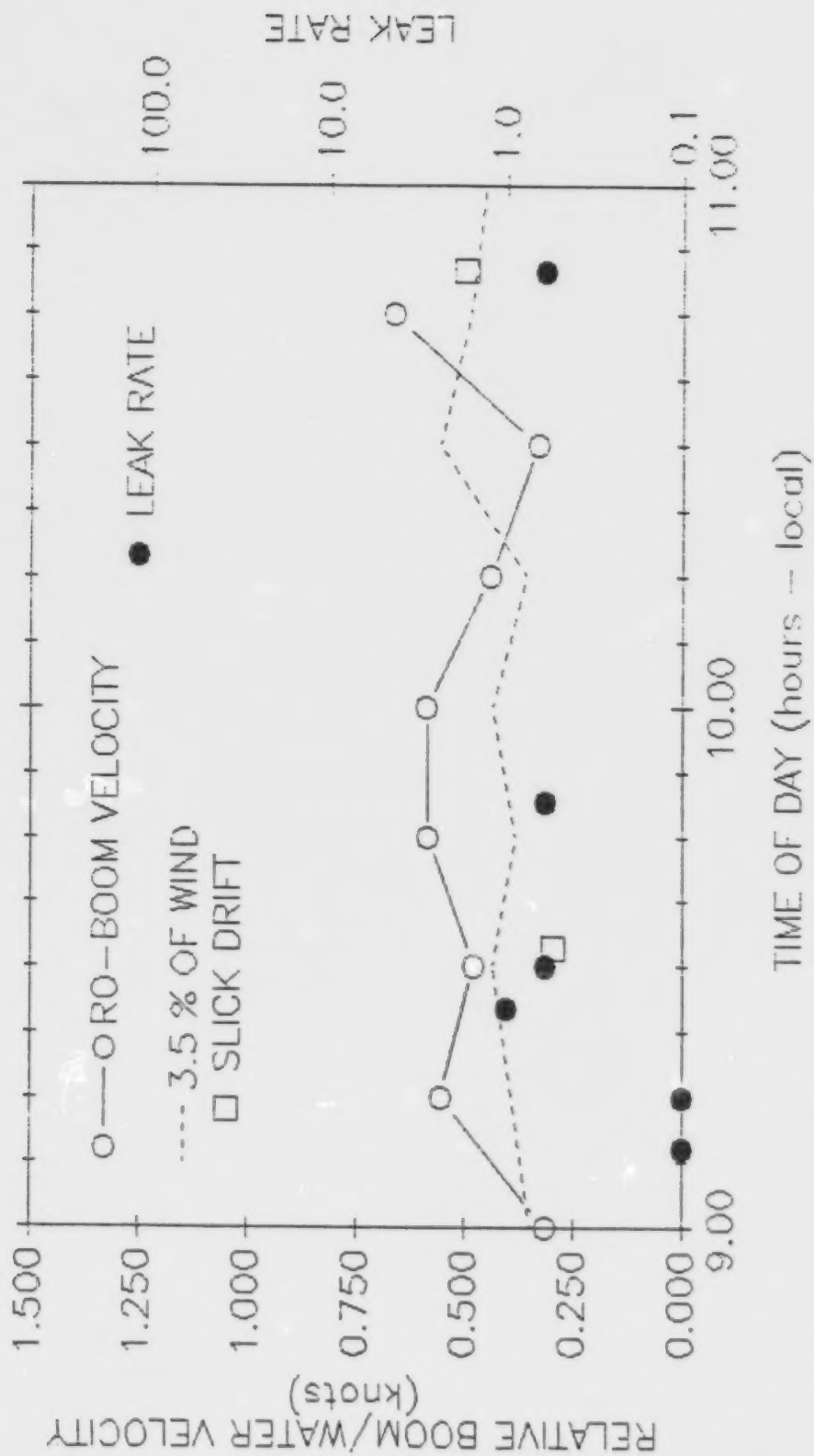




Figure 10 — Leakage of sheen past RO-BOOM; note very little oil against boom

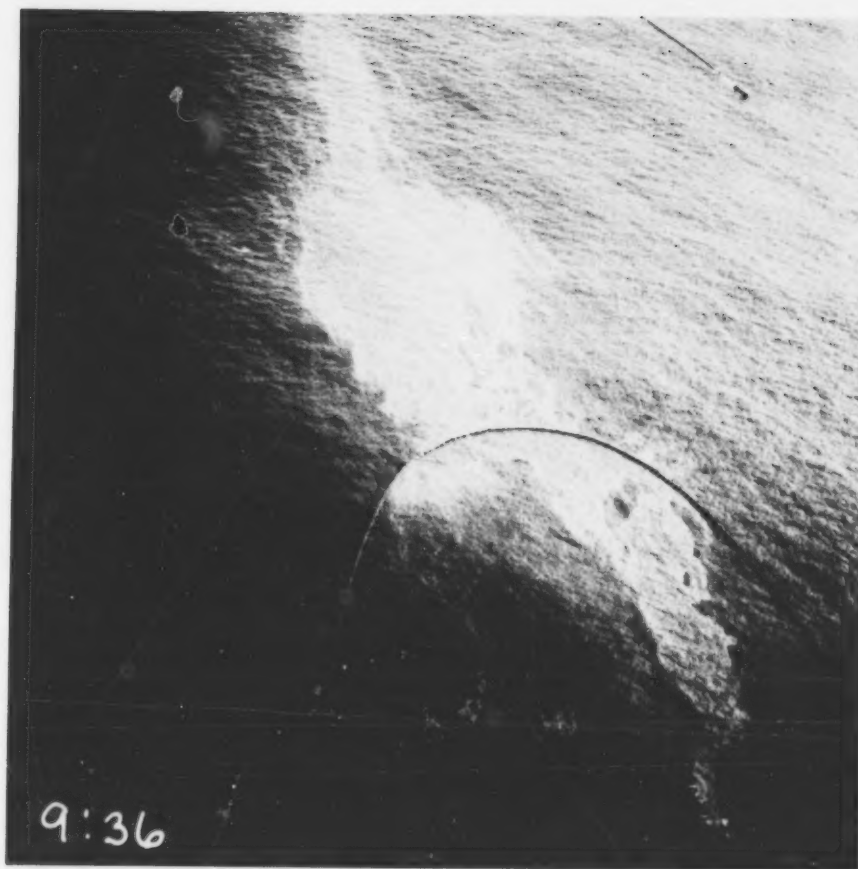


Figure 11 — Greater leakage of sheen past RO-BOOM; note change in width of sheen due to increase in volume of oil contained compared to Figure 18

that the slick thickness was reasonably constant. As noted previously no testing to first loss, by increasing speed, was conducted with the RO-BOOM though splashover losses were noted by personnel in a small boat near the end of the test.

Figure 12 shows a comparison of relative RO-BOOM/water velocity and oil leak rate during the skimmer trials. Relative water velocities were higher at this time than during the morning test since the tow vessels were now heading downwind and needed to move faster to maintain steerage. Visually estimated leak rates were slightly higher (1 to 2) than previous (0.5 to 1). The evening leak rate data could be grossly underestimated as surface vessels to windward of the skimming vessel reported considerable numbers of emulsion balls in the sheen emanating from the skimming operation (Figure 13). It is possible that some or even all of this emulsion may have been driven beneath the boom by the cooling water discharge from the skimming vessel when it impinged on the oil in the boom.

Vikoma Ocean Pack Figure 14 compares the leak rates and relative boom/water velocities for the period of time before, during and after the test of the Vikoma Ocean Pack. Wood chip drift time data for both tow vessels is available only for a 45 minute time period during the actual boom tests. Drift velocities from the tow vessel CCGS Grenfell are plotted as an indicator of relative boom/water velocity before and after the test however, as can be seen by comparing the Grenfell data with the calculated data from both vessels during the test period, there can be a considerable difference between the two. Prior to the test the Grenfell data is likely an underestimate of the actual velocity since during this period the other tow vessel was manoeuvring while the Grenfell maintained station. The roles reversed after the test and thus the Grenfell data for this period probably overestimates actual velocities.

Prior to the test, when the Vikoma boom contained only very small volumes of oil and velocities were low, the relative leak rate was on the order of 0.1 (Figure 15). After intercepting the oil released from the OHMSETT instrumented boom at about 1330 the boom contained about 300 m^2 of oil with a reported visually estimated thickness of 2 to 5 cm translating to some 6 to 15 m^3 of oil. At this time the relative leak rate was 1.0 (Figure 16) with a relative boom/water velocity of 0.25 m/s (0.5 knots).

The phenomenon of the Vikoma boom creating a small breaking wave at the juncture of the air and water chambers was observed. This likely causes some dispersion of oil beneath the boom but the rate would be very low. In booms full of oil this wave would likely be damped out. Previous tests with the Vikoma boom have reported a phenomenon where these waves prevent the slick from touching the boom; this was not observed in these trials. As the tow vessels manoeuvred the Vikoma Ocean Pack into a "J" configuration the relative velocity increased to in excess of 0.5 m/s (1 knot) and the relative leak rate increased dramatically to 200. Even this number may be conservative as visual estimates of the slick trailing the boom gave thicknesses of 3 to 4 mm or relative leak rates of 600 to 800. All the oil was lost from the boom pocket in a period of about 5 to 10 minutes. The cause of the oil loss was slick entrainment beneath the boom (Figure 17); little splashover and no boom sinking or wave topping was observed.

Subsequent to this the tow vessels repositioned heading downwind and recollected some thick oil; leak rate estimates are not available for this time period since it was impossible to distinguish oil emanating from the boom from the oil surrounding the area. During manoeuvring to reform a "J" at approximately 1430 for a second skimming attempt with the Vikoma boom, the relative boom water velocity exceeded oil containment limits and most of the oil was again lost. Following this second effort excessive strain was placed on the boom during manoeuvring causing

FIGURE 12
RO-BOOM LEAKAGE DURING SKIMMER TESTS

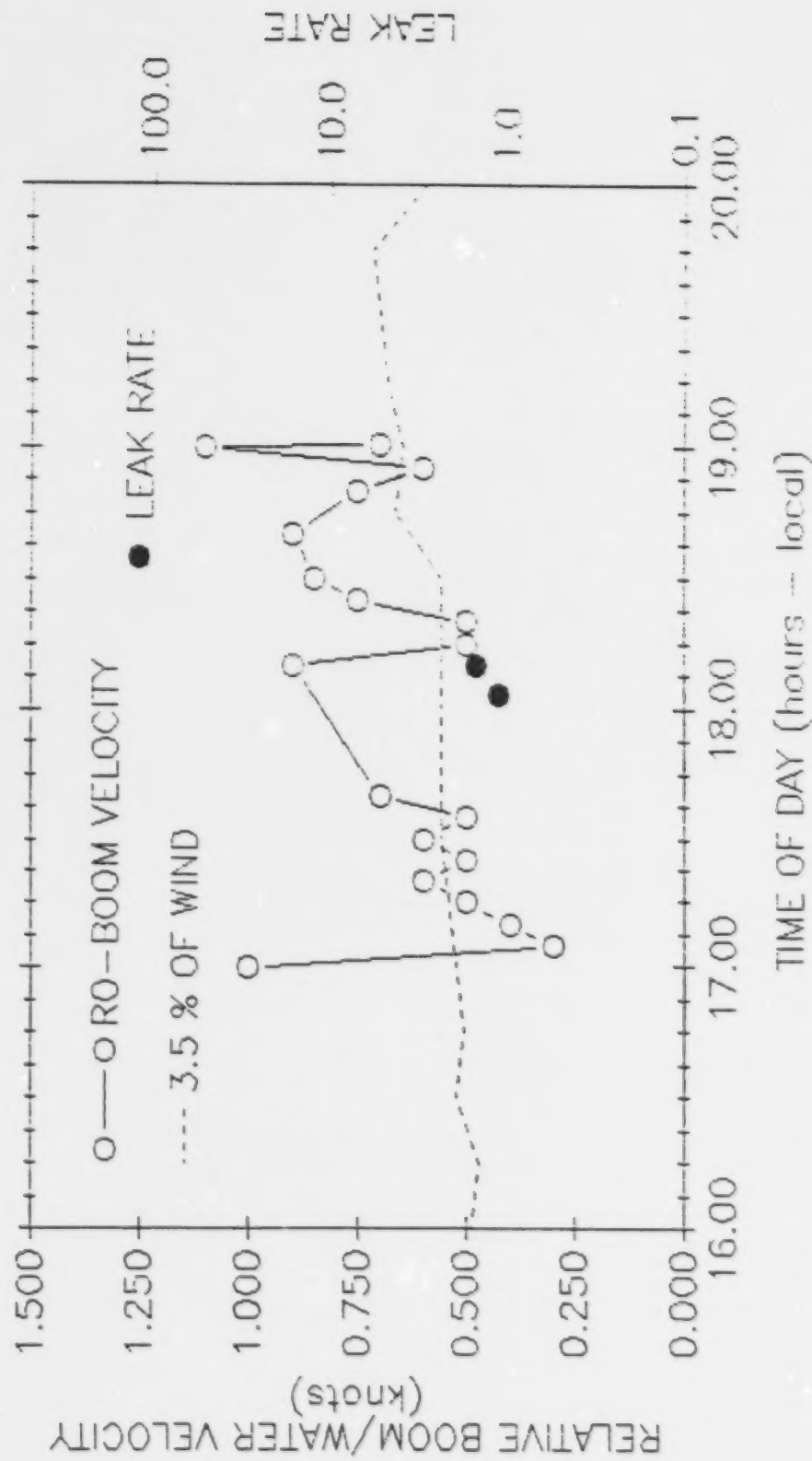




Figure 13 - Oil leakage from RO-BOOM during skimmer trials (compare sheen width to Figures 10 and 11)

FIGURE 14

VIKOMA OCEAN PACK LEAKAGE

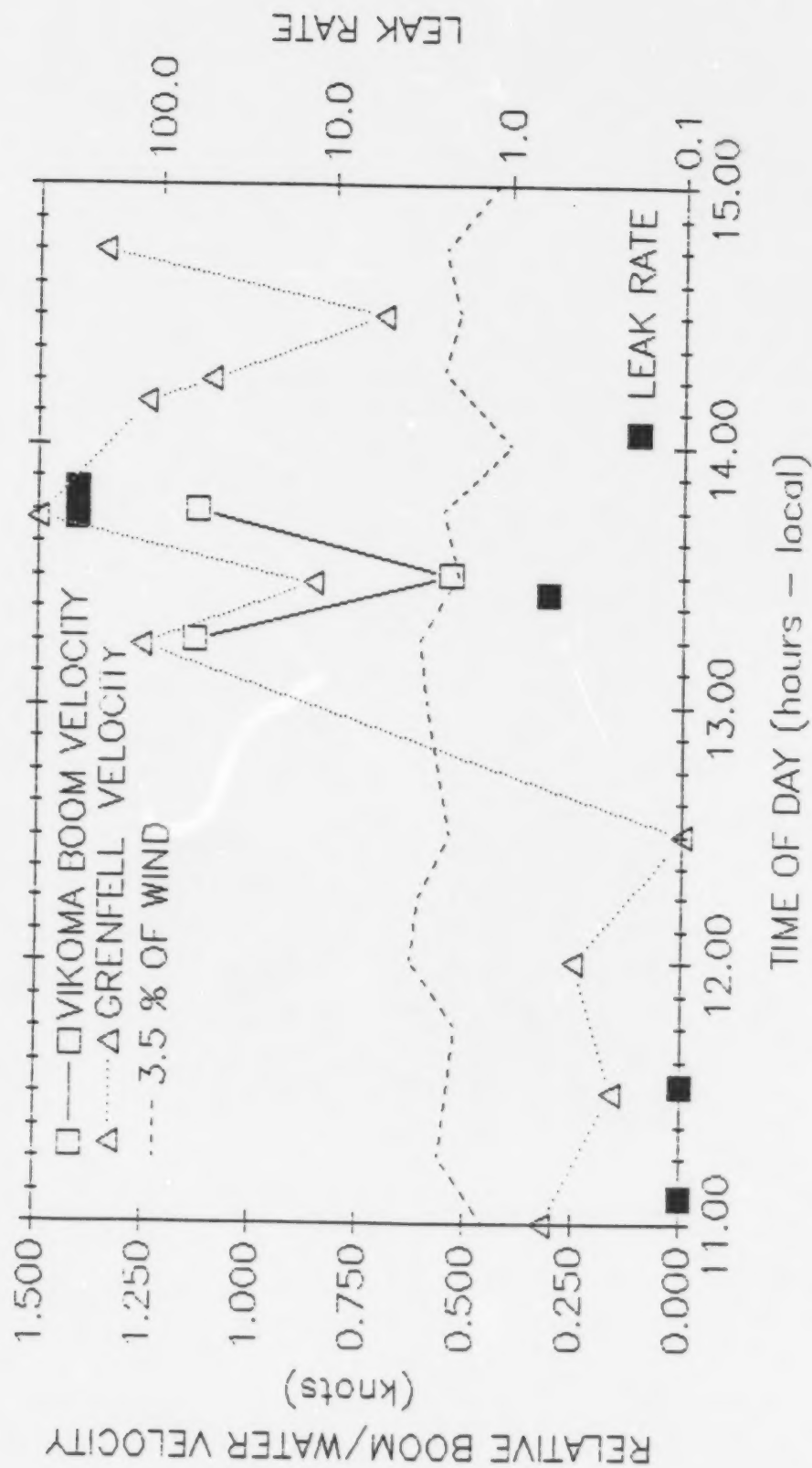




Figure 15 — Vikoma Ocean Pack leakage while containing very little thick oil



Figure 16 — Vikoma Ocean Pack leakage while containing thick oil; note area of thick oil.



Figure 17 — Significant leakage of oil from Vikoma Ocean Pack. Relative boom/water velocity in excess of 0.5 m/s (1 knot)

the boom to lift from the water for as much as 10 m between wave crests on several occasions.

Comparison Figure 18 compares the leak rate and relative boom/water velocity data for both the RO-BOOM and the Vikoma Ocean Pack. Based on the estimated leak rates both booms performed equally well while maintaining station into the wind. The high loss rate from the Vikoma Ocean Pack during manoeuvring into the wind is related solely to the fact that, under the wind conditions at the site, any manoeuvring upwind caused relative boom/water velocities to exceed containment limits ($0.5 \text{ m/s} = 1 \text{ knot}$). This is a factor independent of boom design. It is worth noting that the winds at the test site particularly during the afternoon and evening (15 to 20 knots), were near the maximum operating limits for any containment boom (20 knots) operating in a stationary upwind mode. Wind driven wave heights would also have continued to increase from the last observation of $1.3 \pm 0.2 \text{ m}$ at 1900 hrs to approach the upper limits for boom containment (1.5 to 2 m) by the end of the trials at 2036 hrs.

In general, the RO-BOOM seems slightly more prone to splashover in the upwind mode while the Vikoma boom seems slightly more susceptible to wave-induced dispersion losses.

Both booms were judged acceptable for use offshore; the limiting wind and sea state for their use in containing slicks in a stationary mode, oriented into the wind would be only slightly higher than the conditions encountered during the trials. The booms could be used in still higher wind/sea conditions but only in a downwind mode (as was the case in the late afternoon and evening during the trials). This approach to extending the limitations of offshore containment and recovery (i.e., operating downwind) could be effective when attempting to chase individual slicks but would not prove useful when operating at the site of a stationary oil spill source, such as a blowout, where the objective is to capture the slick as near to the source as possible (by definition by operating into the seas).

Skimmer Performance

Due to the time required to collect sufficient oil for the skimming tests, deteriorating weather conditions, darkness, the addition of Elastol to the oil between skimmer tests, and mechanical difficulties with the Heavy Oil Skimmer, it was impossible to conduct thorough tests of the skimmers that would permit complete evaluation of their effectiveness on spills of waxy crude oils. Regardless, valuable information was collected on the general performance of the skimmers.

Once sufficient emulsion had been contained within the pocket of the RO-BOOM (about 300 m^2 , with an estimated thickness of 10 cm, or 30 m^3 , 7900 gal) the skimmer tests commenced. The results for each skimmer are discussed separately.

Framo ACW-400

Recovery Rates Figure 19 shows the flowrates measured for the fluid recovered by the Framo ACW-400 skimmer. There is an obvious discrepancy between the results from the Venturi meter readings and the results from the tank soundings. Examination of the raw Venturi data (McKowan and Borst 1987) shows that in many of the 3-second data sampling periods, the maximum recorded value is the upper limit of the equipment, thus the 3 second recorded averages, and the 1 minute averages calculated for Figure 19 are underestimates of actual flow conditions. For this reason

FIGURE 18
BOOM LEAKAGE RATES

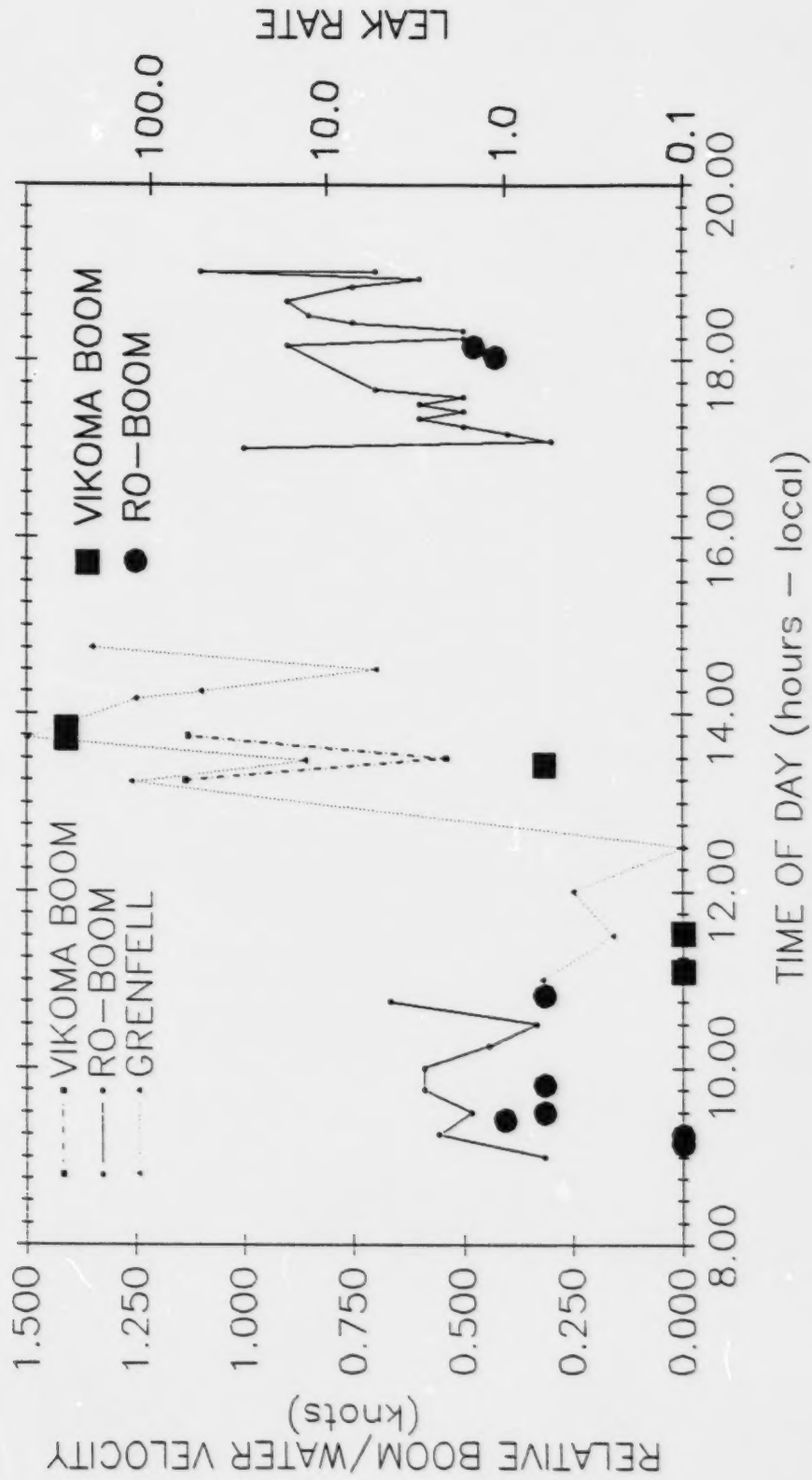
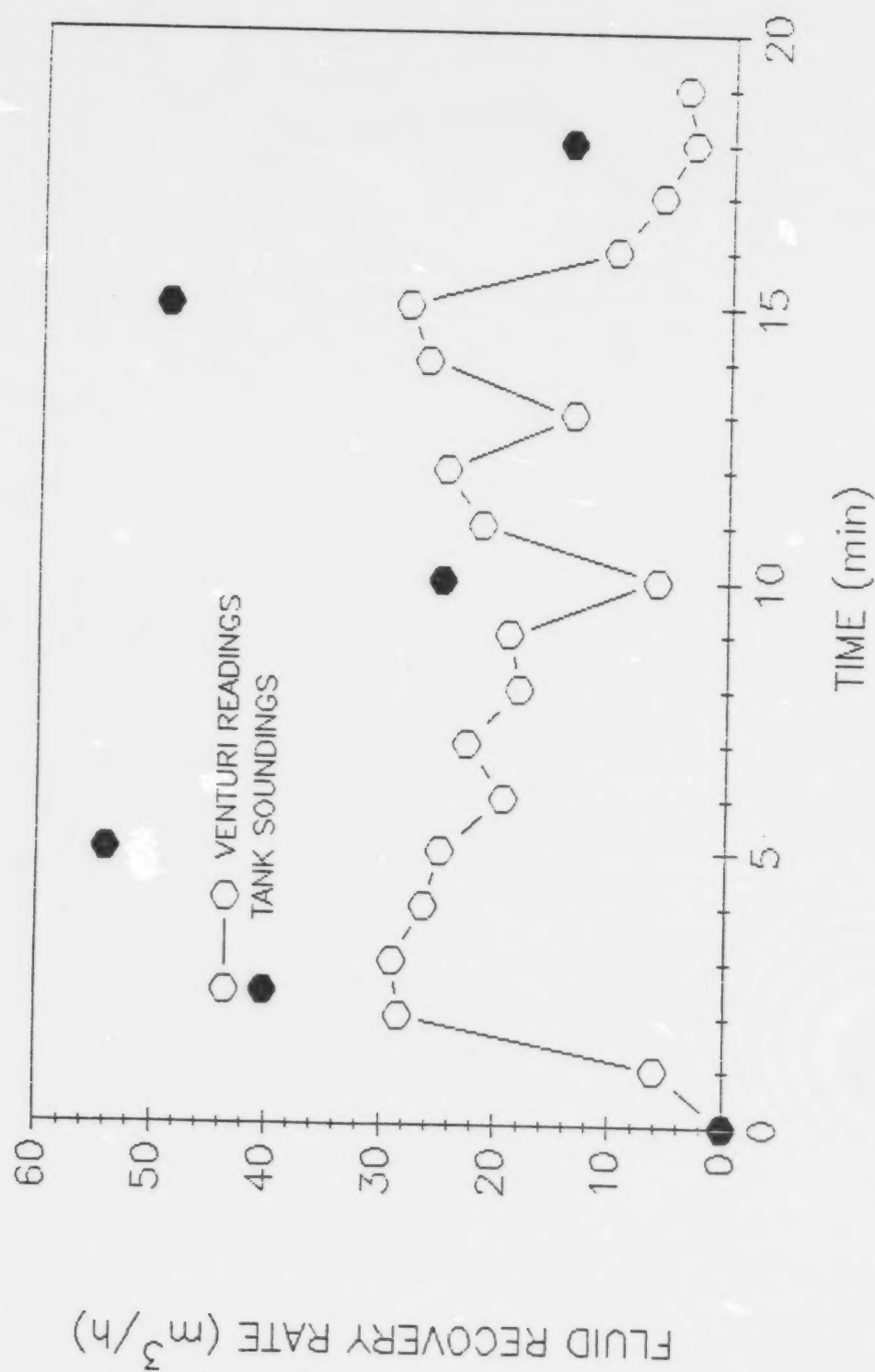


FIGURE 19
FRAMO ACW-400



the performance assessment of the Framo ACW-400 skimmer is based on tank sounding data only. Over the 23 minute test period the Framo recovered some 11.6 m^3 (3065 gal) of fluid at an average recovery rate of $39 \text{ m}^3/\text{hr}$ (172 gal/min). After accounting for 5 m^3 (1320 gal) of free water recovered and 2.5 m^3 (660 gal) of water in the emulsion recovered the oil recovery efficiency for the Framo ACW-400 was 35% ($14 \text{ m}^3/\text{hr} = 60 \text{ gal/min}$). The maximum fluid recovery rate recorded was $54 \text{ m}^3/\text{hr}$ (240 gal/min).

General For the first few minutes of its test the Framo ACW-400 was incorrectly positioned at the outer edge of the oil and was collecting primarily water. During the last few minutes of its test, Elastol was added to the slick; this had no measurable or observable effect on its performance probably because the Elastol had not had sufficient time to act on the oil. During its period of operation it was noted that waves frequently flooded the collection well of the Framo ACW-400 skimming head resulting in the recovery of large volumes of water. Based on observations of the other two skimmers tested in a free-floating mode, it is possible that the oil recovery efficiency of the Framo ACW-400 could have been greatly improved by operation in a free-floating mode rather than attached to the hydraulic arm. Observations of the action of the skimmer head suggest that the motion-compensation in the Framo ACW-400 hydraulic arm can adequately deal with the pitch and roll of the skimming vessel but cannot compensate for shorter period wave action.

Visual observation of the discs during the skimmer test indicated that the waxy oil was not adhering well; unfortunately the Framo ACW-400 was not redeployed and tested after the Elastol had acted on the oil and no comparisons can be made.

GT-185

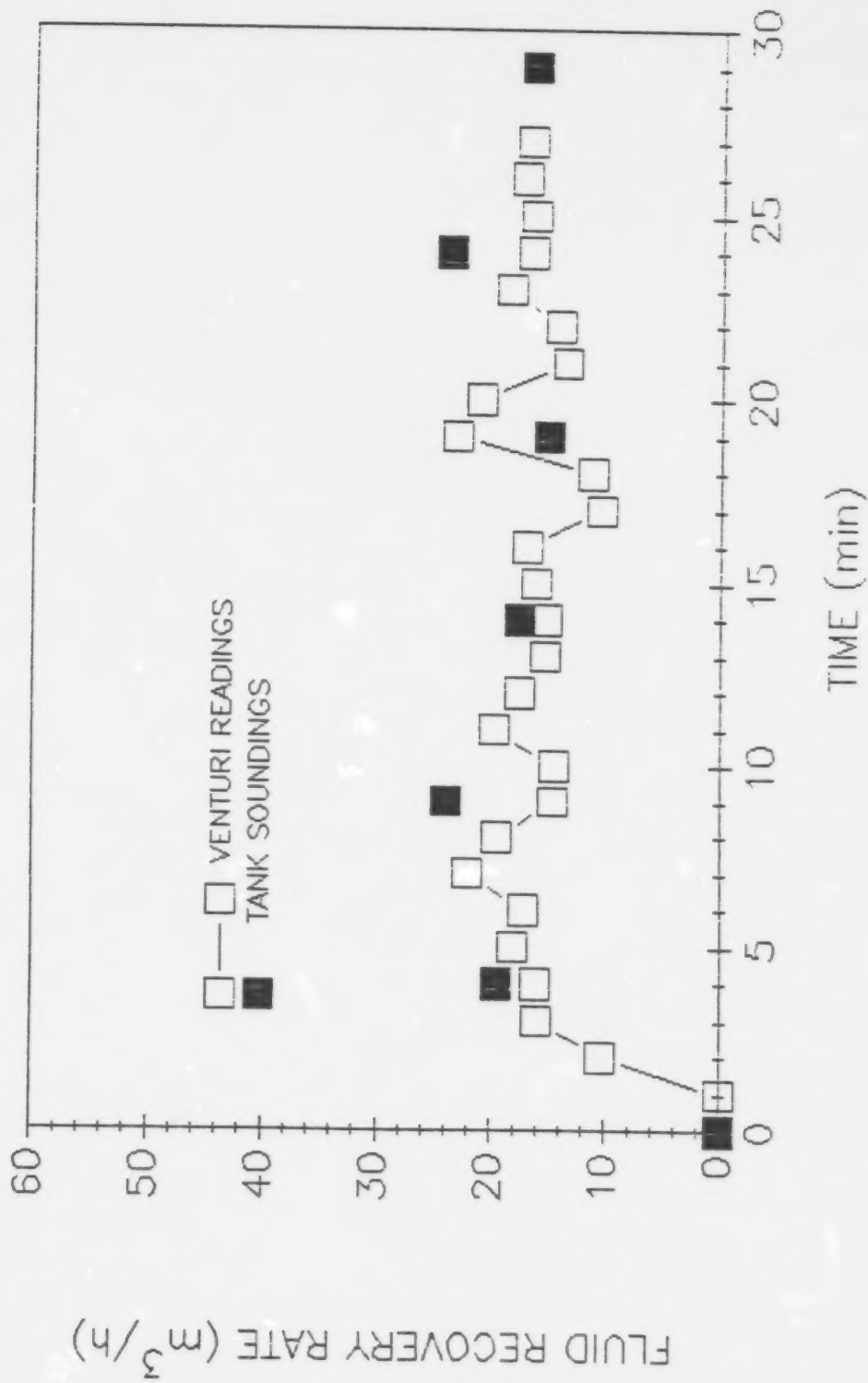
Recovery Rates Figure 20 shows the fluid recovery rates measured with the Venturi meter and tank soundings for the GT-185 skimmer during its test. In this case, since the fluid recovery rates were lower than during the Framo ACW-400 test, the two sets of data correspond well. Over the 29 minute test period the GT-185 collected a total of 9.4 m^3 (2480 gal) of fluid at an average recovery rate of $19 \text{ m}^3/\text{hr}$ (85 gal/min). After accounting for 5 m^3 (1320 gal) of water in the emulsion recovered (no free water was measured), the oil recovery efficiency was 46% ($9 \text{ m}^3/\text{hr} = 40 \text{ gal/min}$).

The maximum fluid recovery rate measured (over a 5 minute period) was $24 \text{ m}^3/\text{hr}$ (105 gal/min).

General Since the test of the GT-185 skimmer took place subsequent to the addition of Elastol to the slick, no evaluation of the effectiveness of this skimmer for the recovery of waxy crude oils can be made. In general the skimmer operated without incident during its test and, due to its free-floating mode, followed the waves very well, as evidenced by the absence of free water in the recovered product. On one occasion the skimmer did snag on the boom when the skimming vessel drifted slightly off station, but the skimmer was undamaged.

The Elastol rendered the oil viscous resulting in high pressure drops in the skimmer discharge and perhaps reducing the performance of this device.

FIGURE 20
GT-185



Heavy Oil Skimmer

The heavy oil skimmer was deployed four times: once into the collapsed "J" formed by the Vikoma Boom and three times during the skimmer tests utilizing the RO-BOOM. Only during the last deployment, in emulsion to which Elastol had been added, was recovery rate data recorded. Unfortunately, this last deployment was cut short when the discharge hose from the skimmer burst.

Recovery Rates Figure 21 shows the Venturi data that was collected prior to the failure of the discharge hose, and the termination of the trials due to darkness and deteriorating weather.

No tank sounding data is available since the discharge hose burst before the recovered fluid filled the hose to the tank. Over the five minute test period the skimmer recovered an average $11 \text{ m}^3/\text{hr}$ (50 gal/min) of fluid. The maximum fluid recovery rate was $20 \text{ m}^3/\text{hr}$ (90 gal/min). It should be noted that this recovery rate was obtained with only one drum of the Heavy Oil Skimmer fully operational; the absorption fabric on the other had been damaged in the previous deployment and only 30–40% of this drum was covered. Based on one sample of unknown origin the oil recovery factor was 35% ($4 \text{ m}^3/\text{hr} = 20 \text{ gal/min}$). No information on the amount of free water vs. water contained in the emulsion is available for this sample.

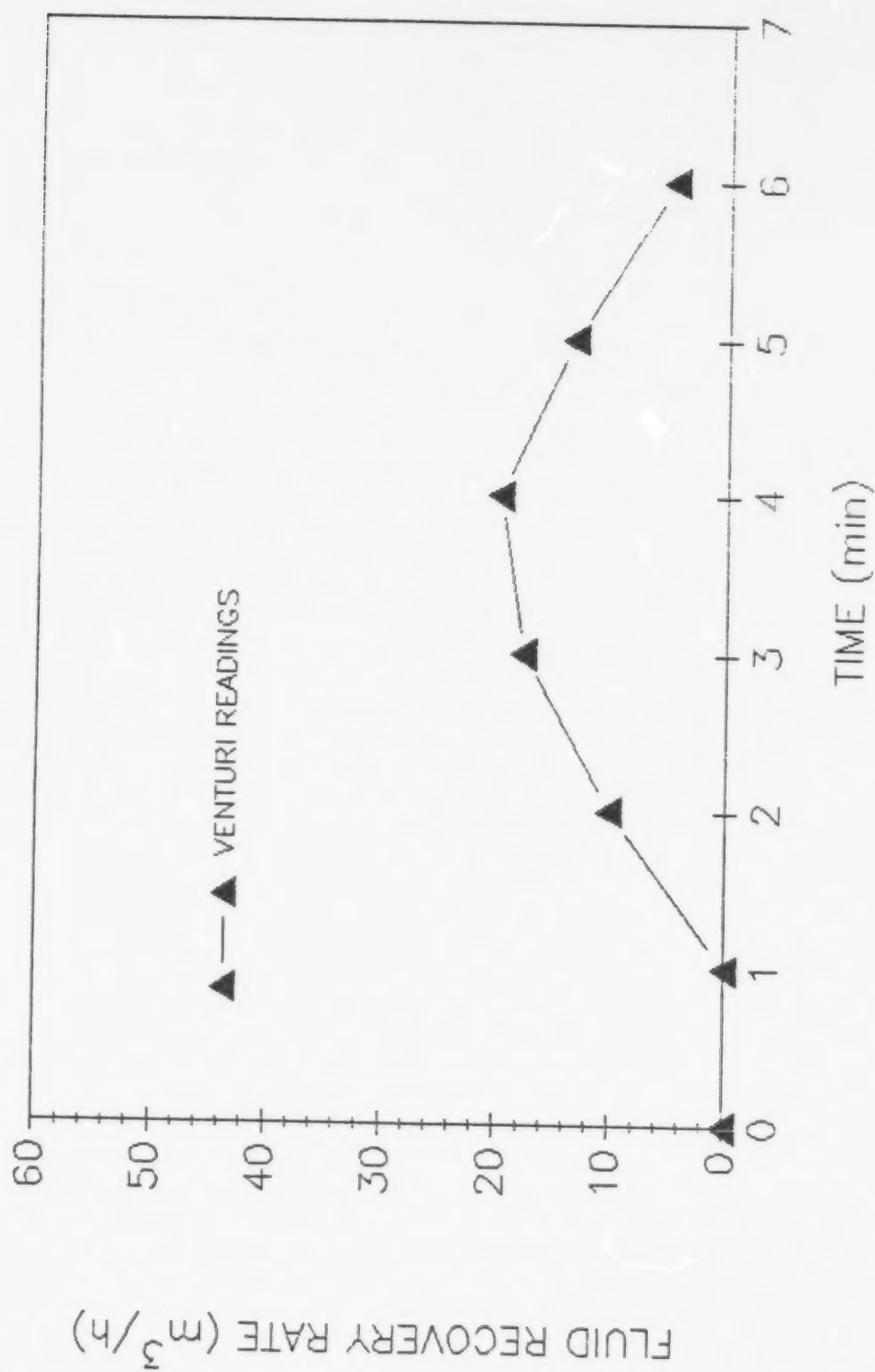
During a previous deployment in the slick prior to Elastol addition, it was observed that very little oil was adhering to the drums of the Heavy Oil Skimmer; no recovery was measured (Figure 35). In comparison, operation of the drums in oil to which Elastol had been added resulted in a layer of oil 1 cm (0.4 inch) or thicker adhering to the drums. One observer noted that the skimmer operated as well or better in the reverse rotation mode (pushing the oil down beneath the drums and up onto the scrapers) as it did in the normal rotation mode (pulling oil up over the top of the drums and down onto the scrapers).

General For the first two deployments of the Heavy Oil Skimmer it was attached to the Framo unit hydraulic arm by means of a universal joint. This caused excessive pitch and roll of the skimmer, causing complete submergence of one roller on one occasion. For the third deployment, the universal joint was replaced by a short length (0.6 m) of rope. This allowed the skimmer to operate in a free-floating mode and follow the waves much better. Unfortunately, the short rope length required that the hydraulic arm remain in close proximity to the skimmer and, during one roll of the skimming vessel the hydraulic arm hit one drum and tore the fabric. For the last deployment the heavy oil skimmer was attached to the hydraulic arm by a much longer chain.

During the first deployment of the Heavy Oil Skimmer (into the pocket of the Vikoma boom) the snagging of the skimmer by the boom caused the failure of a hydraulic hose; this was easily repaired. The third deployment of the Heavy Oil Skimmer was unsuccessful because a bolt had fallen into the pump intake; this was quickly rectified.

Overall, the tests of the Heavy Oil Skimmer were unsatisfactory since insufficient data was collected to evaluate its performance in recovering waxy oil. Further testing is required. In general and based on visual observations, the skimmer seemed to work better in the oil with Elastol added (the skimmer was specifically designed to recover viscous oils such as Bunker C) and followed the waves much better when operated in the free-floating mode as opposed to hard-mounting to the Framo hydraulic arm.

FIGURE 21
HEAVY OIL SKIMMER



Comparison

Although it is impossible to draw quantitative conclusions from a comparison of the skimmers tested since the Framo ACW-400 was tested prior to Elastol being added to the slick, the GT-185 was tested after and the Heavy Oil Skimmer was operating with one damaged drum during its final test, a presentation of the data may prove useful for future studies.

Table 2 and Figure 22 compare the overall average performance measured for the three skimmers. The Framo ACW-400 achieved the highest recovery rate ($39 \text{ m}^3/\text{hr} = 170 \text{ gal/min}$) but much of this was free water. Discounting this, the Framo recovered $22 \text{ m}^3/\text{hr}$ (95 gal/min) of emulsion or an equivalent $14 \text{ m}^3/\text{hr}$ (60 gal/min) of oil. This, of all the tests, is the only one that represents the skimmers ability to recover waxy crude oil. Had the skimmer followed the waves better and been positioned in the thick portion of the oil for the entire test it is likely that the measured oil recovery efficiency (35%) would have been higher, but not dramatically so. The poor adherence of waxy oils and their emulsions to the oleophilic discs of this skimmer type is apparent in the relatively low emulsion and oil recovery rates (previous tests with non-waxy oils have yielded recovery rates in the 50 to $100 \text{ m}^3/\text{hr}$ range). Most of the oil recovered was as a result of the oil slopping over into the sump i.e., the skimmer was operating as a weir device.

In comparison, the GT-185 with a fluid (and emulsion, since no free water was collected) recovery rate of $19 \text{ m}^3/\text{hr}$ (85 gal/min) and an oil recovery efficiency of 46% seemed to be operating near capacity. This was evident from the occasional flooding of the collection well. It is possible that the performance of this skimmer was reduced by the addition of Elastol to the slick; the increased viscosity of the emulsion would reduce both flowrates over the weir lip and pumping rates.

The measured recovery rate of the Heavy Oil Skimmer ($11 \text{ m}^3/\text{hr} = 50 \text{ gal/min}$) is likely an underestimate for the performance of the skimmer in oil with Elastol added for two reasons: first one drum of the skimmer had been damaged resulting in the loss of 60 to 70% of the oleophilic fabric on its surface and second, it is likely that debris found blocking the Venturi throat reduced the pump discharge rate (the resulting backpressure seems the most likely cause of the subsequent failure of the discharge hose) and may have affected differential pressure readings. It is unclear whether this latter factor would result in under- or overestimates of flowrate.

Based on a visual comparison of the thickness of emulsion adhering to the Heavy Oil Skimmer drums before and after the addition of Elastol to the slick it is apparent that the Elastol dramatically improved the performance of this skimmer with waxy oil. This is not surprising since the skimmer was designed to recover heavy, viscous oil slicks such as those resulting from spills of Bunker C.

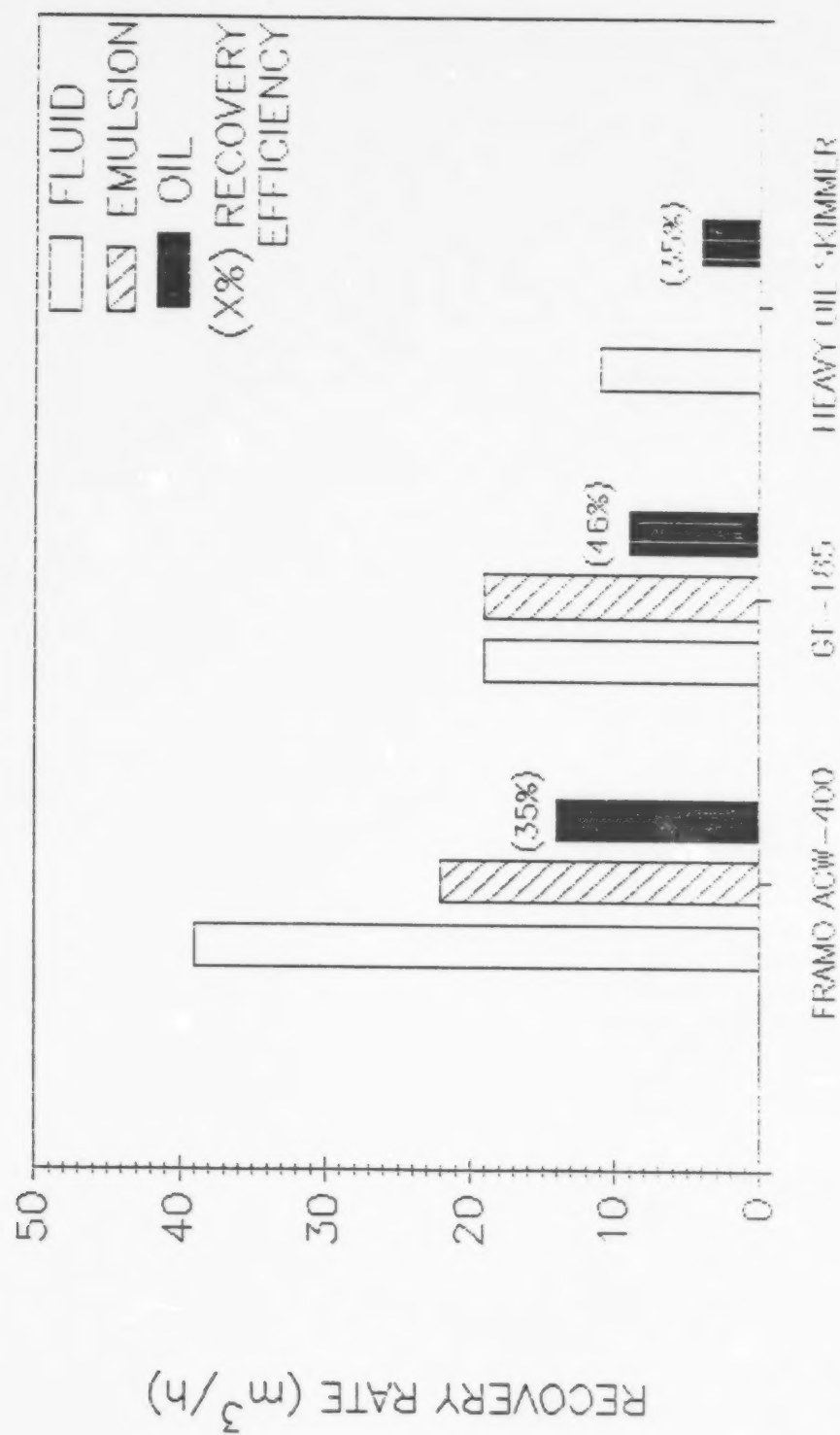
In summary, due to the non-sticky nature of the waxy crude oil used for these tests, the skimmers depending on an oleophilic surface as the collection principle fared poorly. Those utilizing a weir proved more suited to the task. The addition of Elastol to the oil improved the oil's adhesion to the Heavy Oil Skimmer dramatically, but likely detracted from the performance of the weir-type GT-185 skimmer by increasing the oils viscosity and thus flow over the weir and through discharge hoses. This latter observation is important since it is known that some oils discovered on the Grand Banks are much waxier than the test crude and thus will likely be present as very viscous semi-solid mats or droplets rather than the comparatively fluid oil used for these tests (S.L. Ross and DMER 1987). Weir skimmers would likely perform less effectively in the more waxy oils, recovering less oil and more water (S.L. Ross and Hatfield 1986).

TABLE 2
OVERALL SKIMMER PERFORMANCE

SKIMMER	VOLUMES RECOVERED			RECOVERY RATE		EFFICIENCY (vol %)
	FLUID (m ³) (U.S. gal)	FREE WATER (m ³ /vol %) (U.S. gal)	EMULSIFIED WATER (m ³ /vol %) (U.S. gal)	OIL (m ³) (U.S. gal)	FLUID (m ³ /hr) (U.S. gal/min)	OIL (m ³ /hr) (U.S. gal/min)
FRAMO ACW-400	11.6 (3065)	5.0/43 (1320)	2.5/38 (660)	4.1 (1085)	39 (170)	14 (60)
GT-185	9.4 (2485)	0/0	5.0/54	4.4 (1160)	19 (85)	9 (40)
HEAVY* OIL SKIMMER	0	0	0/65*	0	11* (50)	4* (20)

* based on analysis of 6 minutes of venturi data and one oil sample only

FIGURE 22
COMPARISON OF RECOVERY RATES



CONCLUSIONS AND RECOMMENDATIONS

Conclusions

1. Due to delays, deteriorating weather conditions and the addition of Elastol to the slick between skimmer tests (in order to improve recovery rates), it was not possible to draw quantitative conclusions regarding the capability of the skimmers to recover waxy crude oil spills in seas representative of Grand Banks conditions. The Framo ACW-400 skimmer (the only one successfully tested prior to Elastol addition) had an average fluid recovery rate of $39 \text{ m}^3/\text{hr}$ (170 gal/min) with an oil recovery efficiency of 35%. The GT-185 skimmer recovered Elastol-treated emulsion at an average rate of $19 \text{ m}^3/\text{hr}$ (85 gal/min) with an oil recovery efficiency of 46%. The Heavy Oil Skimmer, during one 6 minute test, recovered Elastol-treated emulsion at an average rate of $11 \text{ m}^3/\text{hr}$ (50 gal/min) with an oil recovery efficiency of 35%. Operation of the Heavy Oil Skimmer in the slick prior to Elastol addition resulted in no measurable recovery. Qualitatively, the oleophilic - principle - skimmers were ineffective in the untreated waxy oil. Elastol addition improved the recovery rate of the Heavy Oil Skimmer but likely detracted from the performance of the GT-185.
2. Both the RO-BOOM and the Vikoma Ocean Pack are suited to the containment of waxy oil spills in seas, representative of Grand Banks conditions up to sea state 3-4 and at relative currents less than 0.5 m/s. The Vikoma Ocean Pack boom was deployed and recovered faster and more easily than the RO-BOOM. The RO-BOOM was prone to splash-over of oil at the junction between floatation chambers; the Vikoma boom was prone to oil losses through dispersion by small breaking waves created at the junction of the air and water chambers. Both booms were judged to be equal in terms of sea-keeping and oil retention capabilities.
3. The sea and weather conditions prevalent at the site (sea state 3-4; winds 15 to 20 knots) represent the upper limit of stationary containment operations oriented into the wind. By operating in a downwind mode to reduce relative boom/water velocities and skimming in the lee of a vessel, recovery operations were possible in seas of 1.5 m and winds in the 10 m/s (20 knot) range, equivalent to sea state 4-5.

Recommendations

1. Further testing of the skimmers with waxy, viscous oils is strongly recommended to determine their capabilities.
2. The use of Elastol, and its effects on recovery operations and the environment, should be investigated further.

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PRELIMINARY RESULTS OF THE
VERIFICATION OF OFFSHORE OIL SPILL
CONTAINMENT BOOM PERFORMANCE EVALUATION
PROTOCOL¹

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INTRODUCTION

An oil spill boom is a floating wall used to contain oil or other pollutants that float on water. Consisting of a floatation section and a skirt attached below, a boom may be subjected to all of the conditions water surfaces are known to present. The forces from fluid currents, waves, and turbulence each make booms less and less effective for collecting or containing the floating layer.

Over the past twenty years a number of parameters have been studied to evaluate boom performance. In 1969 Lehr and Scherer divided the parameters affecting boom performance into four major groups; they were: physical properties of the boom, hydrodynamic properties, mooring conditions and environmental conditions. These major groups had a total of twenty seven parameters including such qualities as the tensile and shear moduli.¹ Also in 1969, Wicks specified the parameters that are significant to the interaction of floating oil and the water it is floating on.² Both Environment Canada,³ the U.S. Environmental Protection Agency, Minerals Management Service, and other OHMSETT Inter-agency Technical Committee member organizations have been seeking ways to quantify boom performance. Data collected since 1975 at the U.S. EPA - OHMSETT Facility have been reported in terms of tow speeds at first oil loss and gross oil loss. In addition, booms were tested for stability in water currents, calm water,

1. Although the information described in this article has been funded wholly or in part by the United States Environmental Protection Agency under Contract No. 68-03-3450 to Roy F. Weston, Incorporated it has not been subject to the Agency's review, and does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

sinusoidal waves and harbour chop. Parameters reported by the OHMSETT personnel over the years have not specifically addressed the boom behavior in engineering terms that relate to boom construction.⁴ Moduli and moments of inertia of a boom, as suggested by Lehr and Scherer, are beginning to enter the evaluation scheme in the symptomatic manifestation called wave conformance.

An effort is now underway to systematize the testing of oil spill booms. Using the knowledge gained over the past twenty years a "Test Protocol for the Evaluation of Oil-Spill Containment Barriers" is being established.⁵ The required testing is designed as two separate phases. The first phase is a series of tests to be conducted in a test tank. These tests document the oil holding abilities of the barrier. The second phase designates open-water testing. These tests measure the wave conformance capabilities of the barrier. Open water tests do not use oil although the tests reported here do involve oil being spilled incidental to the tests.

The present discussion is about the reaction of a boom to water surface wave motion and the resulting deterioration of oil holding ability; and specifically, about testing an oil boom at the OHMSETT Facility and in the open ocean off Newfoundland.

BASIC ELEMENTS

Water, Wind, Waves, and Currents

Waves in the open ocean result from combined driving forces. Waves are initially created by wind blowing across the surface of water. The size of the waves depends on how long in time (duration), how great an uninterrupted distance across the water (fetch) and how strong the wind blows. Waves that are created by a wind can out run the wind that caused them. These waves become known as "swell". The swell from one weather system then combines with the wind driven waters of another weather system creating a mixture of wave patterns.

Accurately observing, measuring and reporting the wave condition in open water therefore requires separation of the wave pattern into its component parts. Wave records often take the form of a height measurement (the water surface) over time at a stationary point. In order to make the wave record meaningful (in terms that can be used to engineer or evaluate), frequency spectrum are calculated using Fourier analysis to describe the sea surface's wave components. Such analyses produce a frequency based rather than a time based relationship with the amplitude of the waves.

Repeated measurements of the sea surface height at one location over time results in a collection of amplitude spectra, each spectra possibly different from the others. A sea condition that is consistent enough to warrant a characteristic spectrum is assigned that character by determining the variance of the amplitude spectra. Variance involves the square of the amplitude. Since the square of the amplitude is proportional to the energy, one way of regarding the variance of the amplitudes

of the Fourier components is to call it the energy spectrum.⁶

The surface currents that can be induced by winds as well as the orbital "currents" within waves are major causes of lost oil when oil booms are used to contain floating pollutants. Two parameters used to evaluate a boom in moving bodies of water are: first loss tow speed and critical tow speed. First loss tow speed is the relative water current velocity between a boom holding oil and a water body when oil droplets first shear from the contained oil mass and escape beneath the skirt of the boom. The critical tow speed is the relative current velocity between the boom and water when the boom either submerges or planes. Table 1 lists the ranges of these two parameters (in Meters per Minute) measured at the USEPA-OHMSETT Facility between 1975 and 1982. The effect of waves in reducing performance is significant. Harbour chop (random sea) reduces the critical tow speed by 60% from calm water conditions according to this historical perspective.

TABLE 1. 1975-1982 OHMSETT DATA RANGES FOR THE TWO MOST IMPORTANT MEASUREMENTS OF BOOM STABILITY

	: CALM :	REGULAR* :	WAVES HARBOUR CHOP :
Critical Tow speed (M/sec)	: 0.5 - 1.91 :	0 - 1.14	: 0 - .76 :
1st Loss Tow Speed m/sec	: 0.1 - .57 :	0 - .56	: 0 - .38 :

*Regular means sinusoidal, a monochromatic wave used to measure responses to specific waves

The Interaction of Booms, Waves, and Oil

In July of 1981 and June of 1984, tests were run on what was then known as the Albany Oil Fence (presently the Globe Oil Fence). This oil barrier was not selected for any specific characteristics other than it was available and had a high tension modulus. The 1981 tests established a Boom Loss Measurement Protocol. Figure 1 graphically displays the functional relationship between the loss rate from the boom and the tow speed through calm water.

In 1984 this same style boom was used to evaluate instrumentation designed for measuring boom motion as a response to sea surface wave motion. The study paralleled the type of analysis that goes into the determination of a response amplitude operator (RAO) for ships.

The response a ship exhibits to the wave motion of an "...irregular sea can be represented by a linear summation of its responses to the components of the sea." "...The significance of the principle of superposition [the linear summation] is that if

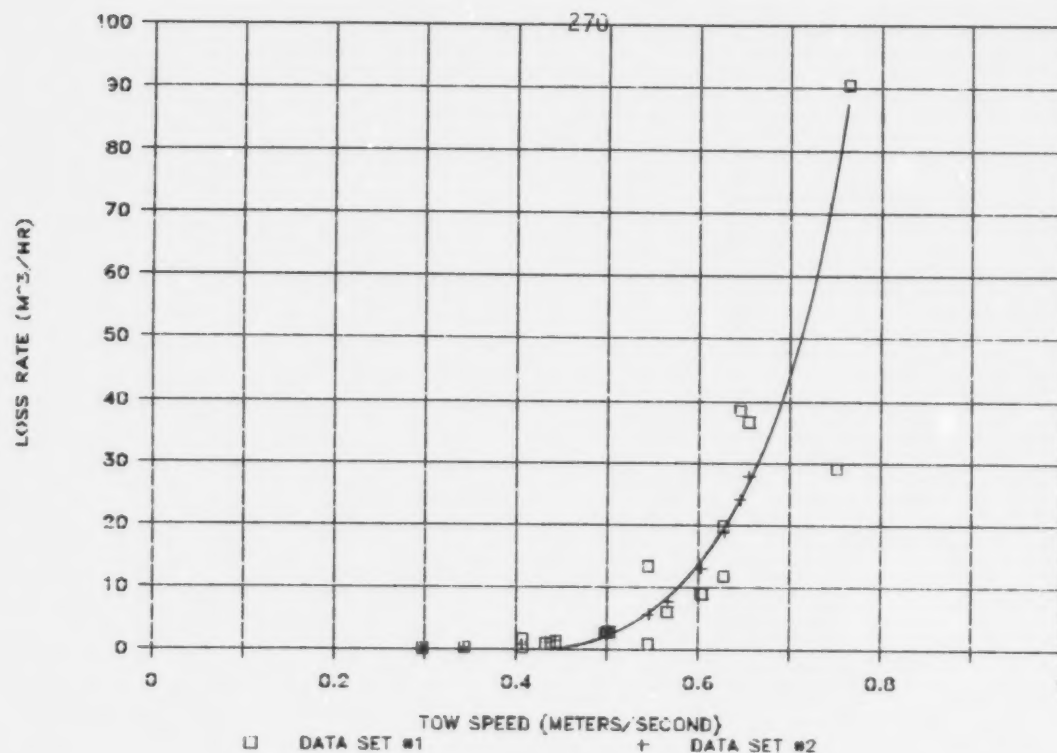


Figure 1. Oil loss measurements made at the EPA-OHMSETT facility. The device was an "Albany Oil Fence"

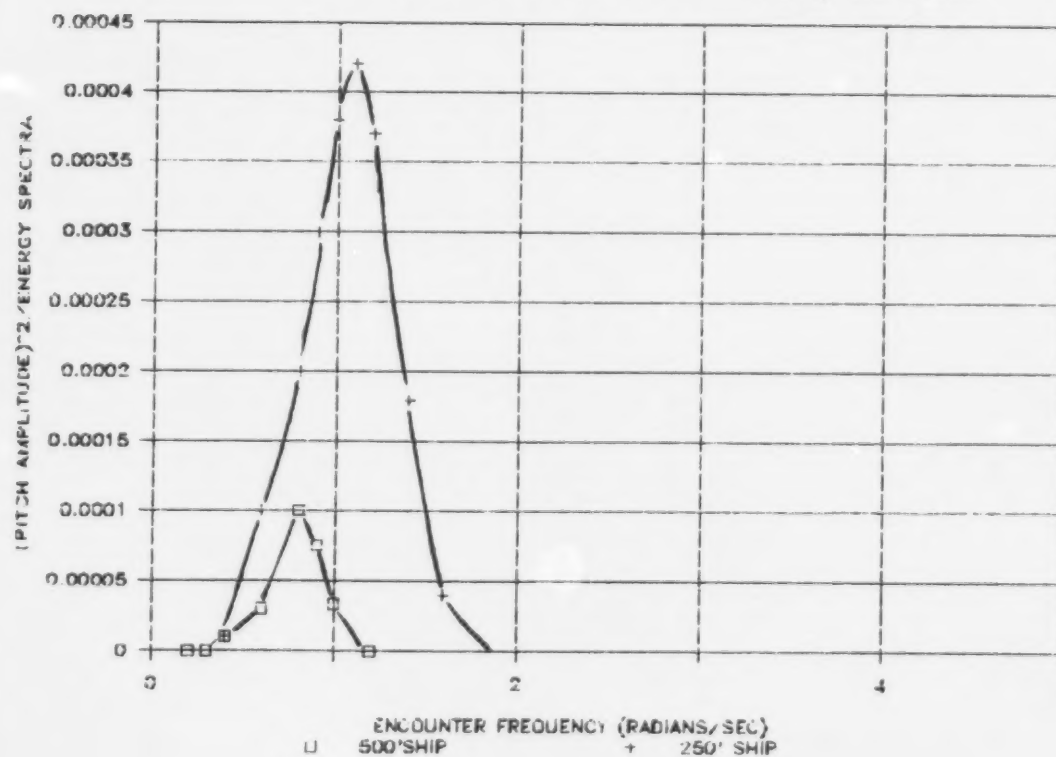


Figure 2. Examples of pitch response amplitude operators for two ships.

we know the ships response to the component waves as determined either by calculation or by model tests, we can predict the behavior of a ship in any actual or imagined seaway, described by its energy spectrum".⁸ As discussed above the seaways energy spectrum is the squared amplitude of waves that exists over the frequency range. A convenient way to represent the response of a ship to a wave is to square the amplitude of the response and determine the ratio of the squared response amplitude to the wave energy at the specific frequency response amplitude operator. Figure 2 is a graph of response amplitude operators for two ships (reference 8). The encounter frequency ω_e is in radians per second ($\omega_e = 0.4$ is equivalent to a wave period of 15.7 seconds).

By applying a similar approach (the emphasis is on similar) to the motion of an Oil Fence in monochromatic wave forms we determined a boom RAO (BRAO). In this case, the amplitude of the Fence was the depth of the skirt below the surface of the water as measured by pressure. By definition zero amplitude was the pressure defined depth (P) at rest in calm water. The water surface amplitude (W) was measured using an ultrasonic transponder mounted above the surface of the water.

The boom was towed in a catenary configuration. Strip chart traces of the measured amplitudes over time were used to obtain P and W. See Figure 3. From these values we made a plot of $(P/W)^2$ versus the encounter frequency. The plot, appearing in Figure 4, demonstrates that the Oil Fence starts to overtly react (not conform) to the water surface at frequencies above 2 rad/sec. In terms of wave period that is equivalent to three seconds and shorter.

Open Water Verification of the Tank Testing

The four basic measurements required to verify the tank tests and in part verify the Boom Test Protocol are: tow speed, oil loss, sea spectrum, and boom response. In the trials tow speed was measured using wood chips and a stopwatch along side one of the tow vessels. Oil loss was visually estimated. Unfortunately during the test a twist developed in the boom causing a gross oil loss. Also unfortunately, sea spectrum data was to have been electronically generated. However, the system failed to function. Pressure sensed boom response data was digitally recorded via data loggers.

The tow speed measurements were made during those times when the tow vessels were properly aligned and towing the boom within the prescribed tow speeds. These values varied between .24 and .55 meters/sec. Predicted oil loss from Figure 1 at these speeds is zero. Yet significant oil loss was occurring as reported by observers even before the twist developed. It is quite probable that the oil was lost during the maneuvering required to establish, intermittently proper alignment and speed. One vessel was designated to hold course while the second vessel would do all the maneuvering. One of the test crew, who has twelve years experience in small vessels in the open ocean, and was on the maneuvering vessel, estimates that speeds up to 2.5 meters/sec

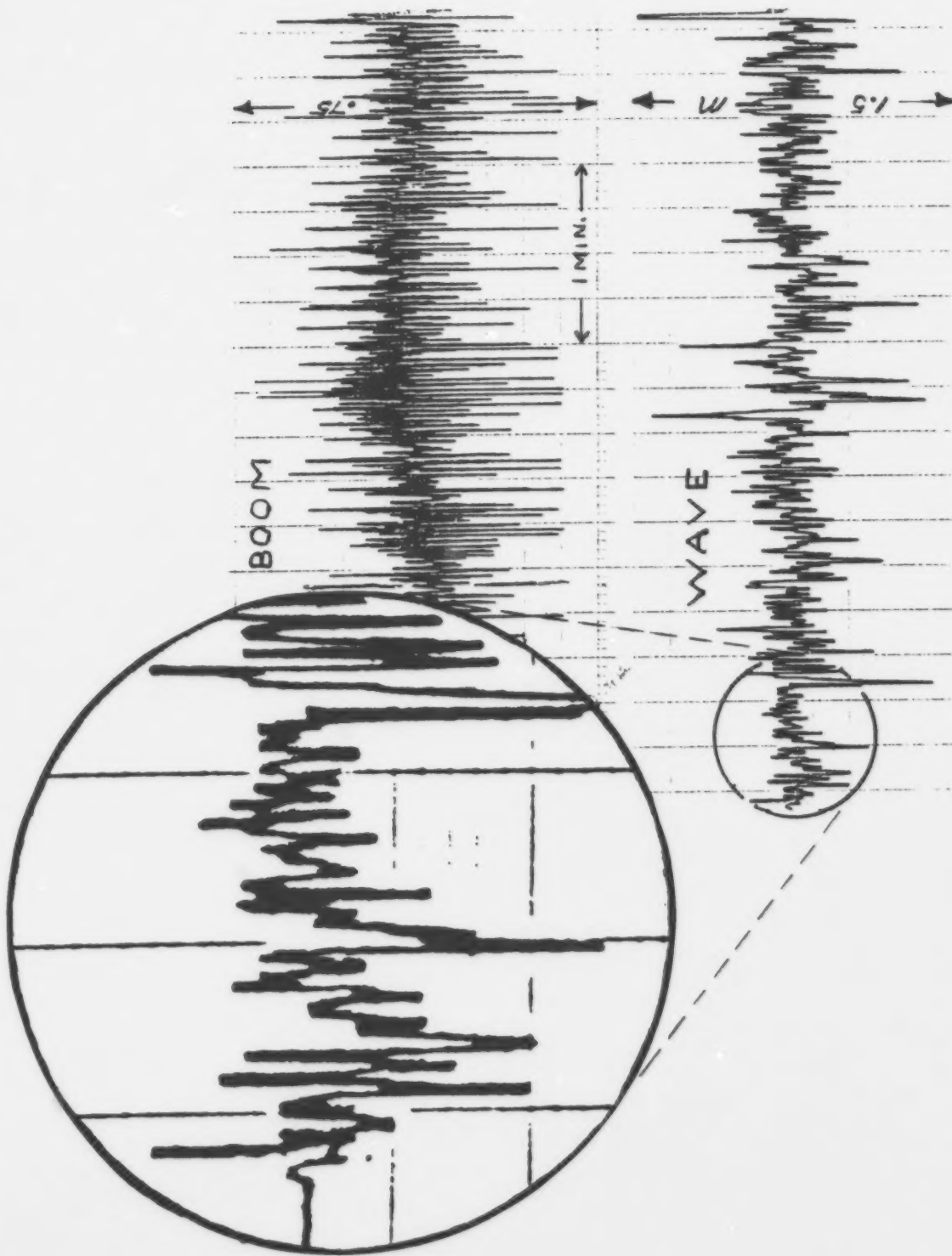


Figure 3. Trace of a boom response to a wave as sensed by a pressure gauge mounted on the bottom of the boom "skirt."

were achieved.

The sea conditions have been reported by visual observations from several observers, both in the smaller tow vessels and in the larger support vessels. The sea consisted of a swell, 1.5 to 2 meters in height at 5 to 7 sec periods (1.25 to 0.9 rad/sec) and wind driven waves, 0.5 to 1.0 meters in height at 3 second periods (2.1 rad/sec). According to the RAO, as defined in Figure 4, the boom should show little overt response to these

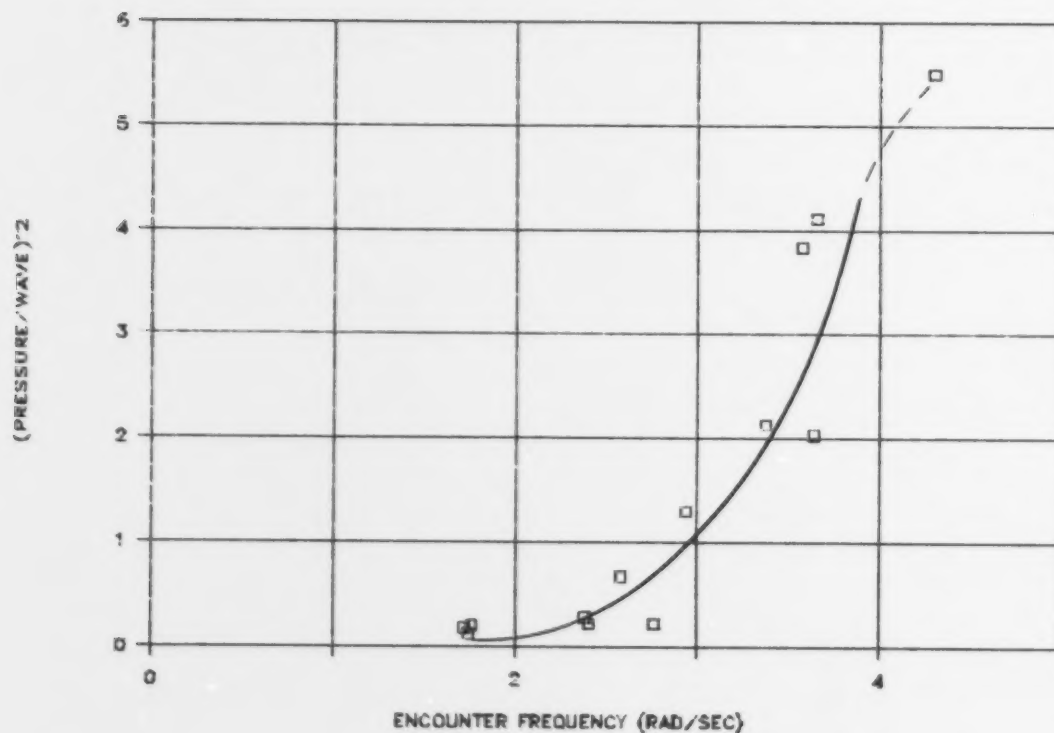


Figure 4. "Boom Response Amplitude Operator", Note the difference in response frequency in Fig. 2 also the y-axis should be noted as different.

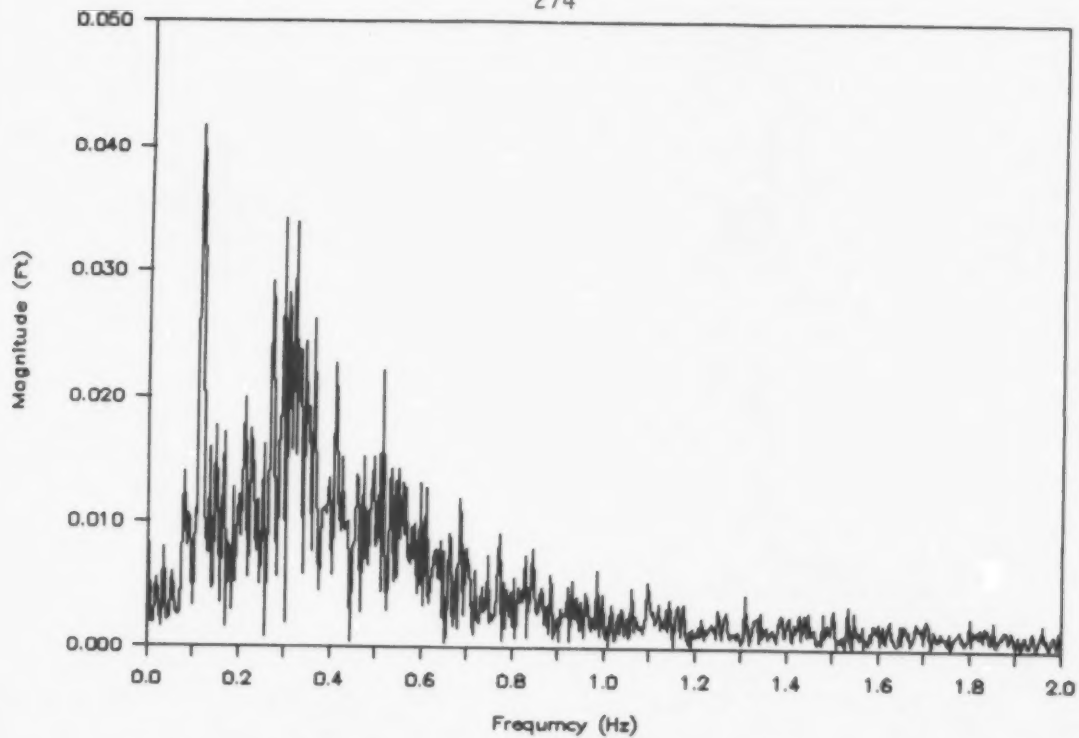


Figure 5. Example of amplitude frequency spectrum for 1987 off-shore boom test.

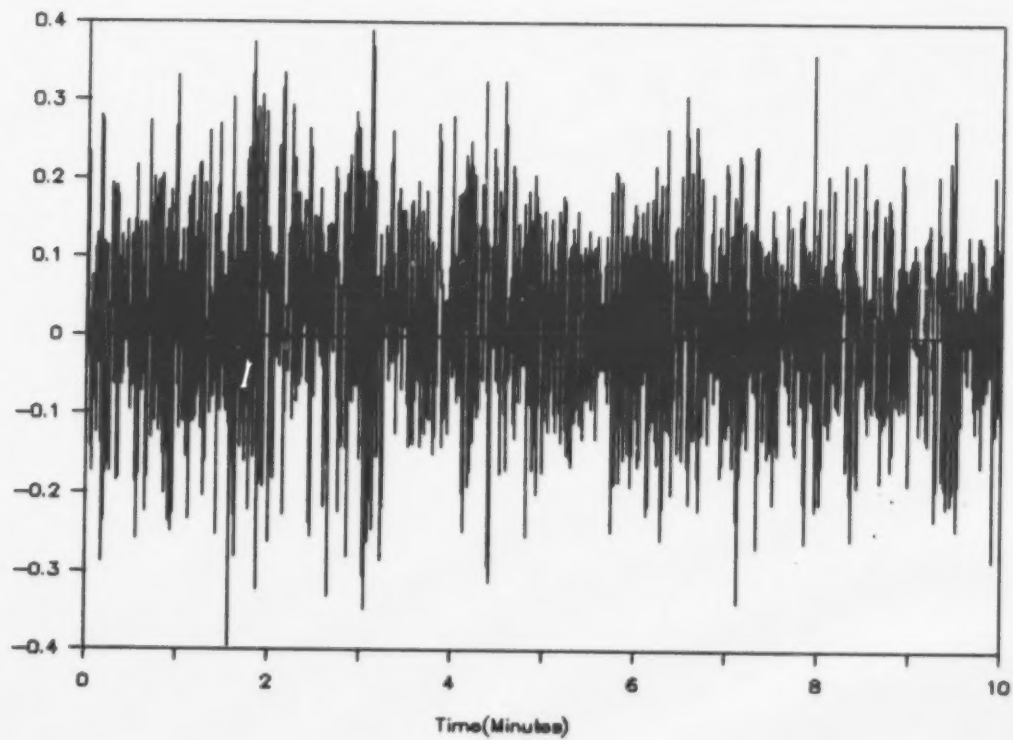


Figure 6. Example of boom amplitude time tracing for the 1987 off-shore boom test.

waves. In other words, the boom should be conforming to the waves.

A graphical printout of a Fourier transformed time record taken during the test shows almost noise level response from the boom as sensed by pressure at the bottom of the skirt. See Figure 5. The ordinate in Figure 5 (the y axis) is presented in feet. The highest value is 0.04 ft. which is 1.2 centimeters at 0.75 rad/sec. The cumulative amplitude of the boom response was between 12 and 24 centimeters according to the "pressure defined" wave record (See Figure 6). Oil in the boom also contributed to the booms conformance by reducing the high frequency components as oil will do. The oils effect can be seen in the photo presented in Figure 7. Notice the loss of chop at the boom apex in the foreground.

Conclusions

The Boom Test Protocol element involving BRAO and wave conformance was verified for the sea conditions encountered during the sea trials. Although the Protocol does not call for the spilling of oil at sea, this "spill of opportunity" was used to verify the tank testing of first loss tow speed. This aspect was not verified, due primarily to the maneuvering difficulties created by the sea conditions that caused boats to respond but not the boom.



Figure 7. Sea surface condition at the boom with oil present.

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LASER IGNITION OF OIL SPILLS: TELESCOPE ASSEMBLY AND TESTING

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ABSTRACT

A technique for using two coupled airborne lasers to heat and ignite Arctic oil spills has been described in previous AMOP presentations. Outdoor demonstrations have proven the ability to ignite cold crude oil in a simulated Arctic environment, and an engineering design has shown the viability of mounting the needed equipment in a helicopter. We have now assembled the telescope required to focus the pulsed "igniter" laser from a helicopter hovering at an altitude of 20m. Ignition has been demonstrated at slant ranges between 20 and 30m, with the lasers directed outward from the platform at angles between 0 and 48 degrees from the vertical. A passive technique provides the capability to automatically focus the telescope.

INTRODUCTION

In the event of an Arctic oil spill, either from a shipwreck or maritime well blowout, it is envisioned that oil reaching the surface of an ice field melting during springtime will form tens of thousands of pools, each having typical dimensions of a few tens of meters.¹ The technique of choice for removing these pools before they transform into unremovable tar is to set each afire within a few days of its appearance. Due to the remote location of the potential accident, ignition of the oil must be accomplished from an airborne vehicle. To date, only pyrotechnic ignitors² have been able to achieve this task. Unfortunately, these devices have shelf lives of only about 5 years, and production of sufficient stock to clean up one major spill could require a recurrent cost of several million dollars. The logistics of manufacturing and transporting the thousands of devices to the spill site have yet to be addressed.

During the past 4 years, a novel dual-laser approach to starting oil pool fires has been developed. After initial theoretical and laboratory studies^{3,4} a ground demonstration of the technique was performed outdoors in conditions simulating an Arctic environment.⁵ Following that success, a helicopter deployable system was designed.⁶ Testing of certain critical aspects of the optical components within that design is currently underway.

BACKGROUND

The laser ignition process may be summarized as follows: A continuous-wave (CW) carbon dioxide laser is used to heat a portion of the surface of an oil pool to its flashpoint temperature and simultaneously establish a thermal field within the oil which will support the growth of a nascent flame. A focused, pulsed laser beam then provides energy which creates a momentary

"spark" above the oil surface to ignite a fire. The technical advances that led to the success of the technique were: (1) learning the requirements to start a small diffusion flame which is able to both sustain itself and spread over a large pool of cold oil; and (2) determining how to satisfy these requirements using lasers.

A schematic illustration of a one-dimensional diffusion flame is presented in Figure 1. At the surface of the cold liquid is a relatively hot layer from which fuel evaporates and mixes with the air above. Combustion occurs in a very narrow layer located a small distance above the surface of the fuel, and combustion products such as hot soot and gases rise above this zone. As the fire burns, combustion energy is radiated and conducted through the air back to the oil pool, thus providing the power required to continue vaporization of new fuel and sustain the burning. If this power is insufficient to overcome the heat flux transported to the bulk liquid by conduction and convection, the surface cools to a temperature below that at which sufficient vapor is produced, i.e., below the flashpoint, and the fire extinguishes itself. Thus, the liquid will burn only after several criteria are satisfied: 1) The surface of the liquid must be hot enough to provide a vapor above the surface which, when mixed with ambient air, is combustible; 2) This vapor/air mixture must be raised briefly to a temperature sufficiently high to initiate combustion; and 3) The liquid fuel must establish temperature and flow fields which transport less power into the liquid's volume than a nascent flame is capable of supplying back to the liquid surface.

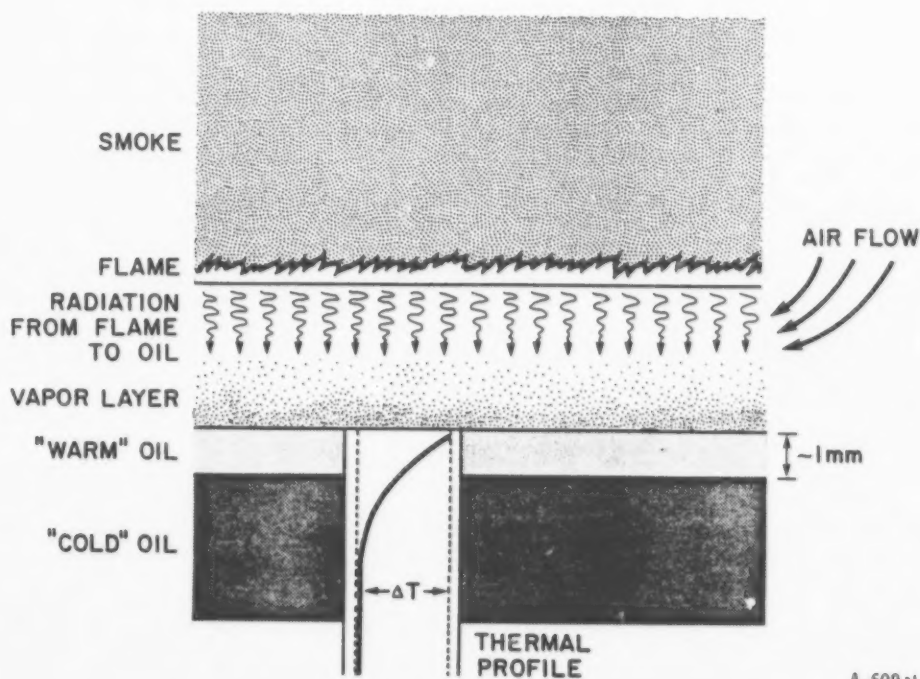


Figure 1. Salient features of a one-dimensional diffusion flame

Cold, aged crude oils fail to inherently satisfy any of these criteria. To generate a combustible vapor mixture, the surface of the liquid must be heated to its flashpoint temperature, typically⁷ as high as 100 C. To ignite the vapor mixture, it must be exposed to a heat source of 700 C or more. The third criteria requires that the liquid absorb a certain amount of energy before the fire is ignited.

Laser beams, which act as remote infrared energy sources, are used to satisfy each of these requirements in the Laser Ignition of Oil Spills (LIOS) technique. By selecting appropriate combinations of laser power, intensity (power/unit area), and irradiation time, ignition of sustained, spreading fires on the surfaces of cold, aged oil pools is accomplished. The powers and intensities delivered by the laser beams are controlled by the choice of lasers and the use of focusing or defocusing optical components. Two lasers are used in tandem as illustrated by Figure 2: A moderate power (< 1000W) CW laser continuously irradiates or "preheats" a small portion of the oil surface thereby establishing the thermal and flow fields required for vapor production and flame survival, satisfying criteria 1 and 3. Concurrently a high power (7 MW) short-pulsed (2 μ s duration) focused laser fires once per second. By focusing this pulsed laser beam to provide a fluence (energy/unit area) exceeding 10 J/cm² at the surface of the pool, its energy is absorbed in the vapor above the oil thereby generating temperatures high enough to initiate the combustion reaction, satisfying criterion 2. When conditions are ripe, the vapor mixture ignites and initiates a self-sustaining fire. Carbon-dioxide (CO₂) lasers have been used exclusively in this technique because of their advanced state of development, energy conversion efficiency, availability and cost. These lasers radiate at a wavelength of 10.6 μ m, in the far-infrared.

The helicopter-deployable version of the LIOS system has been designed with the following features:

1. Can be installed in a Sikorsky S61 or comparable helicopter without affecting airworthiness or safety;
2. Incorporates a CW CO₂ laser producing up to 1000W of power and irradiates the oil pool with the required preheating intensity of 5 to 10 W/cm²;
3. Incorporates a pulsed laser which is focused to provide sufficient fluence to ignite, from a distance, fires on preheated oil pools;
4. Holds the laser beams on target despite helicopter movements and vibrations;
5. Provides sufficient power and cooling capability to operate all of the system components; and
6. Can be operated by an aircraft maintenance technician.

Assuring that the pulsed laser beam is focused at the surface of the oil pool to a fluence which is sufficient to ignite the preheated oil is clearly critical to the success of the system - no spark, no fire. As already mentioned, the fluence per pulse should exceed 10 J/cm² at the oil pool surface. Throughout the experimental development process, this fluence was achieved by focusing the pulsed laser beam with short-focal-length mirrors located within one or two meters of the oil surface. It had not been shown, except by calculation, that sufficient fluence could be provided from a hovering helicopter. This uncertainty has now been resolved, as discussed next.

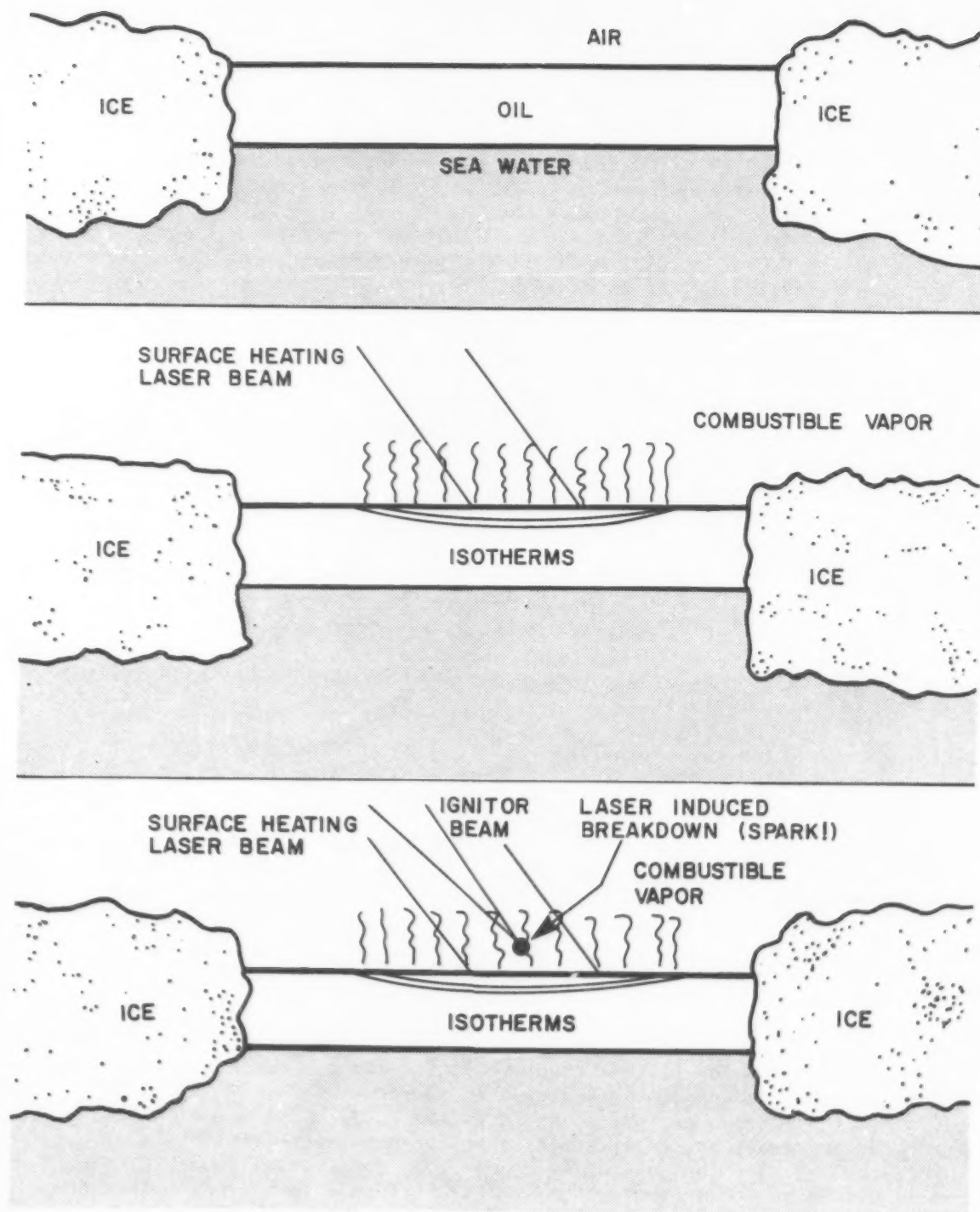


Figure 2. Laser ignition of oil spills concept and sequence

OPTICAL SYSTEM

Design and Layout

A focusing system which meets the mission requirements has now been constructed and tested. In addition to meeting the minimum fluence requirement, the optical system design satisfies certain economic constraints as well as limitations imposed by the CW laser which force the system to operate from a helicopter hovering at a fixed altitude of about 20m above ground level. Individual oil pools are to be selected by pointing the lasers over elevation angles between 0 and 49 degrees, corresponding to slant ranges between 20 and 30m as illustrated in Figure 3. Therefore the pulsed laser focusing system incorporates a capability to alter its effective focal length through these ranges. Furthermore, a means for the operator or automatic controller to determine when the laser is properly focused is included.

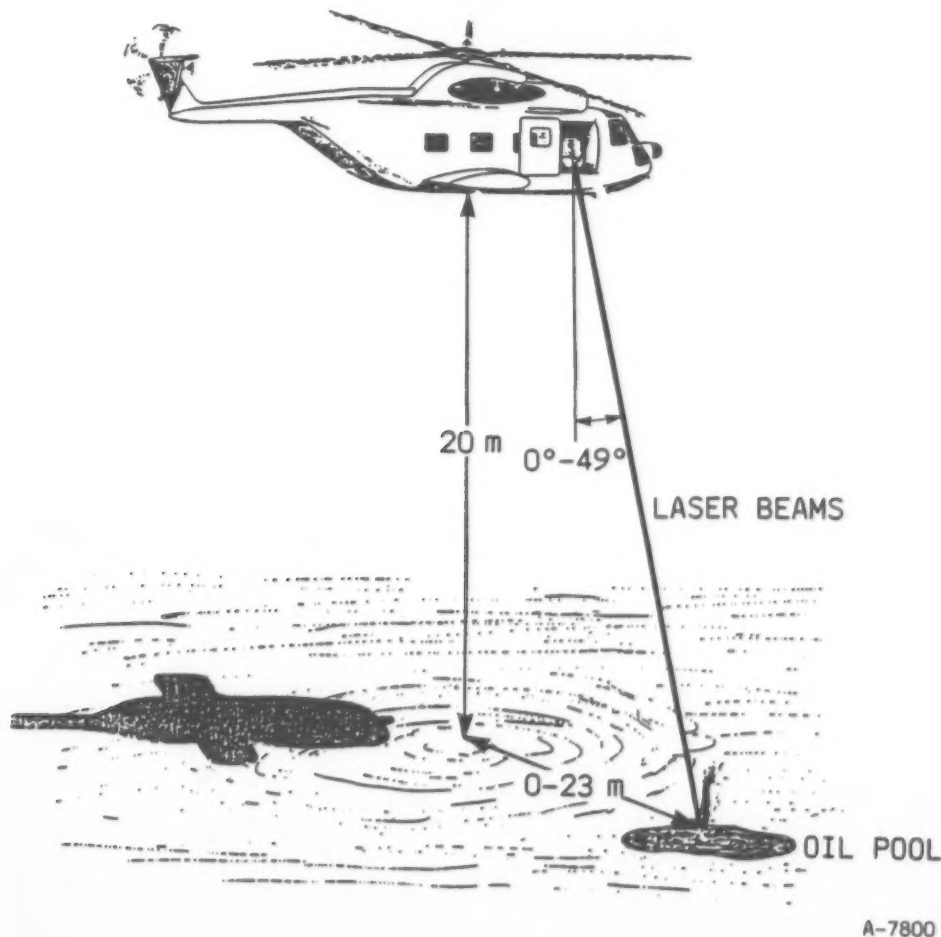
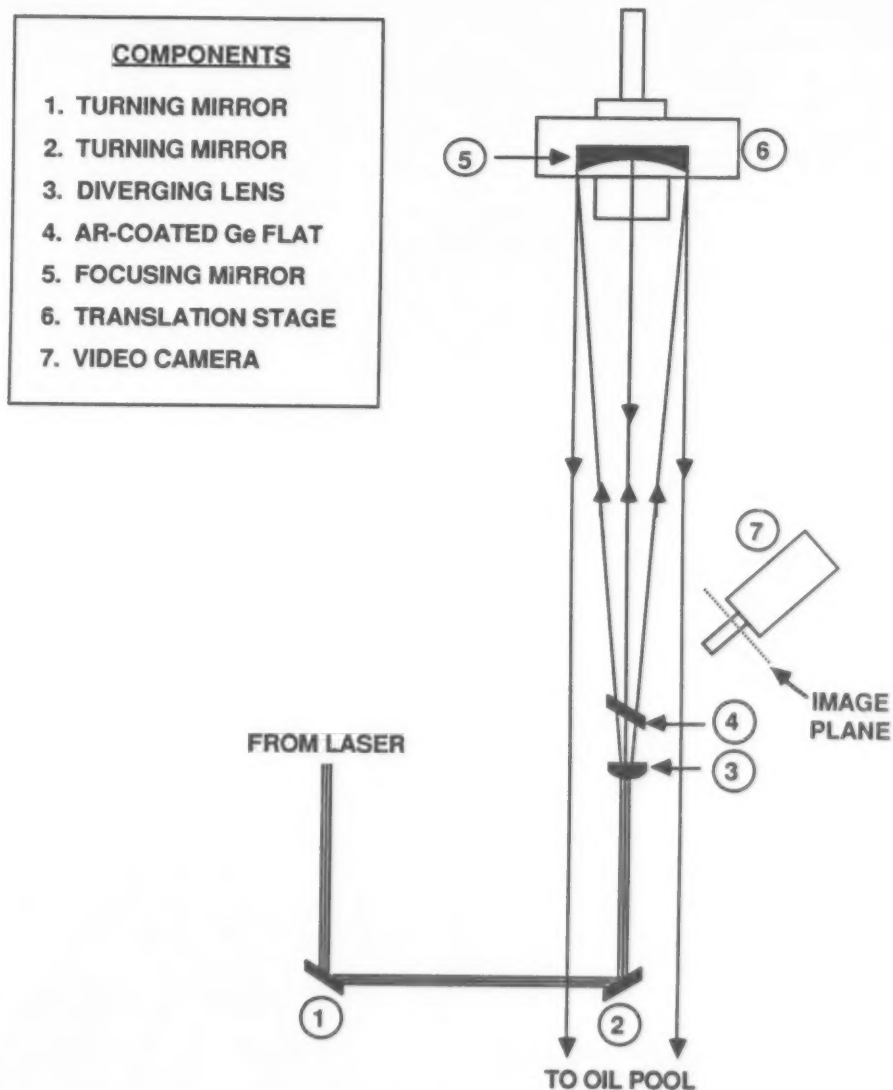


Figure 3. Operational scenario for airborne LIOS system. Not to scale. (Adapted from Ref. 6.)

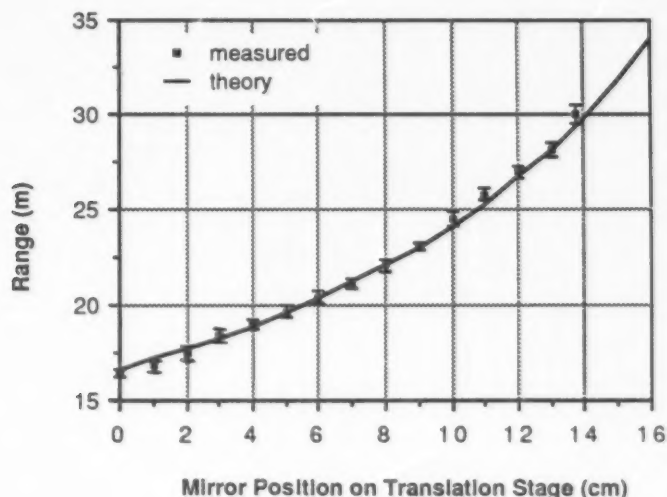
The pulsed laser currently used as the igniter is a Lumonics Model TEA-103 operated in an unstable resonator optical configuration. This laser is nominally capable of yielding 8 J of focusable energy per pulse. To provide a fluence well in excess of the requisite 10 J/cm^2 at the oil surface, the beam is focused to a diameter of about 0.4 cm using a two-element reverse Cassegrainian telescope as illustrated in Figure 4. The laser beam is first expanded by a -35 cm focal length, 2.5 cm diameter concave lens, and then focused by an 80 cm focal length, 25 cm diameter concave mirror. The two elements are nominally separated by 185 cm. The distance from the concave



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Figure 4. Laser-focusing telescope configuration

mirror at which the beam achieves its minimum diameter is the effective telescope focal distance. This focal distance can be varied within the range of 20 to 30 m simply by moving the concave mirror relative to the lens by about 8.2 cm. Figure 5 is a plot of the focal distance as a function of mirror position.



A-8046

Figure 5. Slant range from telescope to oil pool as a function of relative mirror position

The components are all mounted on a single table. The pulsed laser beam is directed into the telescope by small flat mirrors (indicated as components #1 & 2). The beam passes through component #3, the anti-reflection (AR) coated germanium diverging lens and thence passes unaffected through a germanium flat, component #4, also coated so as to be non-reflective at the laser wavelength. The beam then impinges on the focusing mirror (#5) after expanding to a diameter of about 20 cm. The now slightly-converging beam is reflected back along its original path, and exits the telescope. Small flat mirrors direct the focused beam to a simulated oil pool in our laboratory. In a helicopter-based system, larger flat mirrors at the telescope exit will serve the same function.

The concave mirror is mounted on a linear translation stage to facilitate focusing. The accuracy with which it must be positioned is determined by the depth-of-field of the focused beam, defined as the range of distances away from the focal point over which the fluence remains sufficiently high to assure ignition. The telescope is designed to produce, at its maximum range, a focal spot having a diameter which is roughly 1/2 that which is required. (At shorter ranges the focal spot is smaller, i.e., the fluence is higher.) As a result the theoretical depth of field is about 90 cm, indicating that the mirror must be positioned with an accuracy of about ± 7 mm. To determine and control the position of the mirror, it is possible to either: 1) observe an image of the oil pool through the telescope and vary the position of the

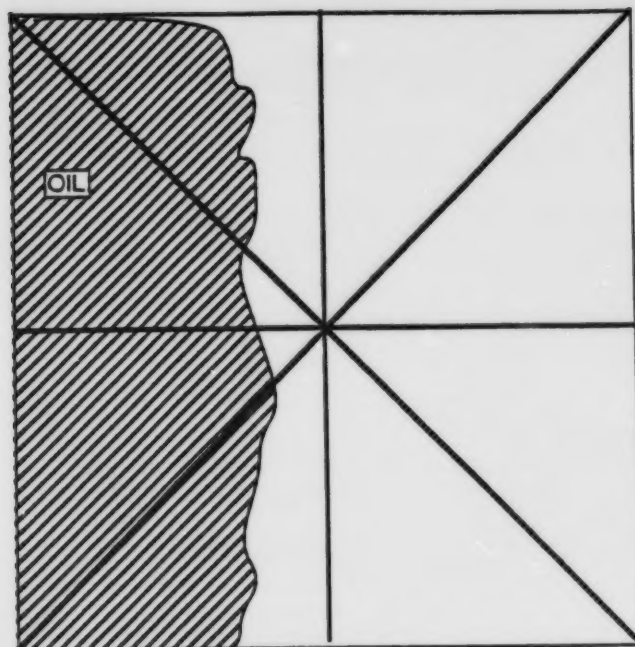
concave mirror until the image is in focus; or 2) measure directly the distance between the telescope and the oil pool and calculate or calibrate the appropriate mirror position. Option A is called passive focusing, while option B active. We are presently exploring the feasibility of employing passive focusing in a helicopter-borne LIOS system.

Focusing Technique

The passive focusing system works as follows: The diverging lens (component #3) causes the pulsed laser beam to effectively originate on a plane located one focal length behind the lens. The telescope images this plane onto the oil pool. By symmetry, an image of the oil pool is formed by the concave mirror at the effective laser origin. This image is comprised of radiation from scattered sunlight and infrared energy emitted in response to heating by the lasers. It therefore has a fairly broad spectral distribution; it contains energy at wavelengths ranging from the visible to the far-infrared. Much of this energy is split from the laser beam's optical path by the germanium flat #4, which, although coated to transmit energy at 10.6 μm without reflection, is highly reflective for wavelengths shorter than about 5 μm . Thus, a visible/near-infrared image of the oil pool is located at the image plane shown in Figure 4. Focusing the telescope is therefore a simple matter of adjusting the concave mirror position until the image of the oil pool is brought into sharp focus.

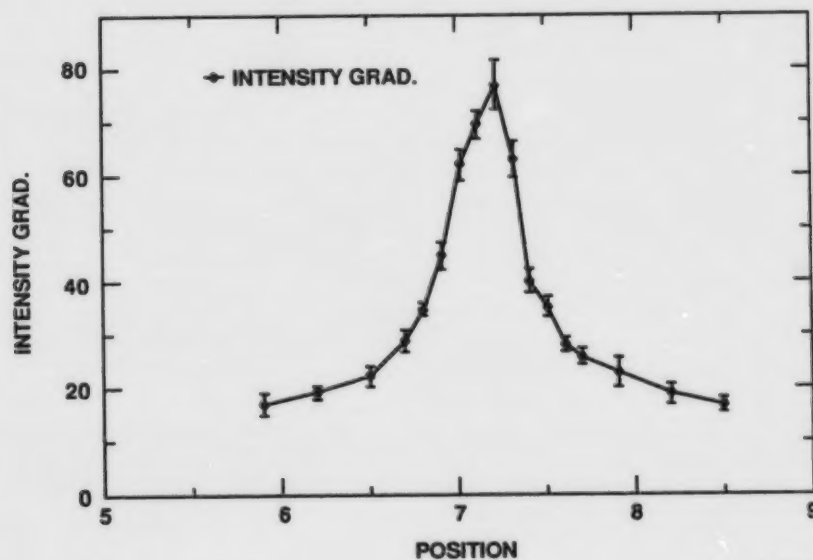
Though this technique facilitates manual focusing, a helicopter-deployable system requires high-speed automated focusing. We are presently automating the passive focusing process by using a computerized image analyzer to determine when the image is at its best focus and employing that information to drive a motorized position controller and move the concave mirror. Images are captured and digitized with a Data Translation Model 2851 Frame Grabber operating within a Compaq 286 personal computer. The frame-grabber generates a two-dimensional array of data corresponding to the brightness or intensity of the image at each of 512 x 512 pixels. These data are processed numerically to calculate intensity gradients along a set of six intersecting lines, as shown in Figure 6. The position of best focus is defined as that position where the average intensity gradient observed along a line within the image is maximized. One of the six lines, that which has the largest gradients and thus contains the features having the highest contrast, is selected for the focus analysis.

To find the optimum mirror position, the telescope mirror is translated along its entire length of travel and the average intensity gradient along the selected line within the image calculated as a function of mirror position. Typical results are plotted in Figure 7. The mirror is then returned to the position corresponding to the peak value of this curve, which is the position of best focus. Tests have confirmed that when the mirror is positioned using this algorithm it is within ± 1 mm of the position which would be calculated from a direct measurement of the distance to the oil pool surface, i.e., the position indicated by Figure 5. Figure 8 compares the calculated mirror positions with those determined using the passive focusing technique. The comparison is seen to be quite good.



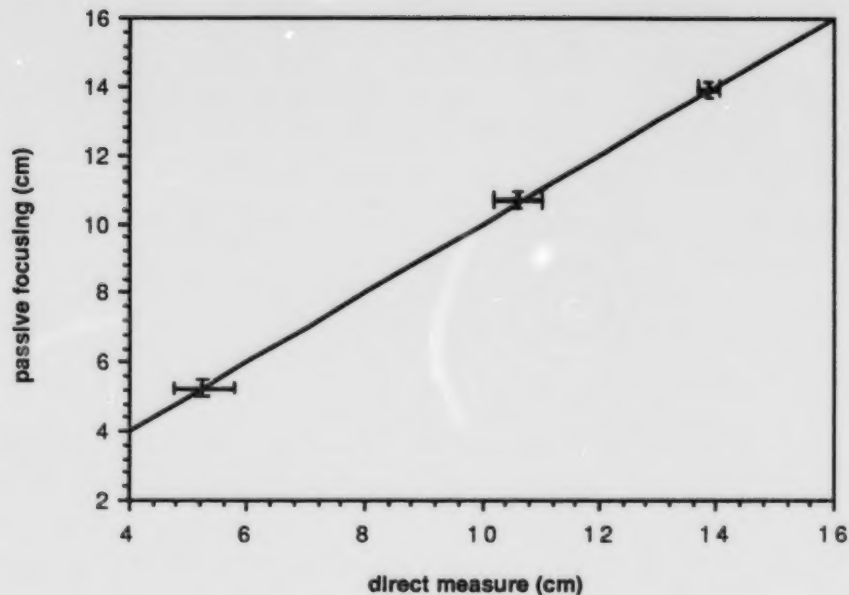
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Figure 6. Illustration of method used to maximize image contrast. Intensity gradients are calculated along the indicated lines



A-7807

Figure 7. Average intensity gradient along a line of image versus mirror position



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Figure 8. Position of concave mirror determined by passive focusing versus position determined by direct measurement of effective focal length

SUMMARY AND DISCUSSION

A laser focusing telescope suitable for igniting oil from a distance of 20 to 30m has been assembled and tested. In addition, a passive technique for focusing the telescope has been developed. This passive focusing algorithm can easily be automated by storing the intensity gradient function in computer memory and programming the computer to drive the mirror to the position of maximum intensity gradient. However, computation of the intensity gradients is rather time consuming. It appears that this method would require several seconds to refocus the telescope after acquiring a new image. This period can potentially be reduced using custom-built analog electronics or a high-speed computer, but both alternatives may be expensive. However, by utilizing active focusing, high speed with equally good precision can be had at what will ultimately be a lower cost. An active system uses a laser rangefinder to continually measure the distance to the oil pool and instruct a controller to properly position the focusing mirror based on precalibrated knowledge of a positioning curve such as Figure 5. Though we are continuing to explore low-cost passive focusing alternatives, we now anticipate that future developments of the LIOS technique will incorporate this sort of active system.

ACKNOWLEDGMENT

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COMPARISON OF RESPONSE OPTIONS FOR OFFSHORE OIL SPILLS

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ABSTRACT

Oil spill response options in an offshore environment generally fall into three major categories: mechanical cleanup, chemical dispersants, and in-situ burning. Each response option can be associated with a specific set of operational, environmental, and oil slick conditions. Pictorial representation of these conditions and related performance characteristics reveal acceptable operating "windows" for each response method. By translating these operational windows into comparative plots of spill access and control rates, one can make meaningful assessments of the relative merits of each response option. Such assessments for major offshore oil spills provide the basis for determining the most effective use of available resources needed for mechanical, chemical and burning techniques.

INTRODUCTION

Any oil spill at sea will be immediately subject to a number of natural processes that will alter the oil's physical and chemical properties. Depending on the type of oil, the magnitude of the spill, and the nature of the environment, these physical and chemical changes may quickly negate the feasibility of using any currently known spill control procedures. The natural spreading of an oil slick, for example, will play a major role in determining which, if any, spill control techniques can be applied effectively. Oil films in a given thickness range may be ideal for chemical dispersants and yet totally unacceptable for burning. A portion of this paper will focus on the significance of oil film thickness in comparing the potential performance of various response options.

Every spill situation is different, and throughout a spill, the conditions affecting the selection of a response mode are constantly changing. A spill's proximity to shore, its areal extent, its age, and its degree of emulsification all influence the choice of the best response technique(s). These and many other changing conditions require that a successful response strategy involve a realistic ongoing assessment of (1) the oil spill's current and near-term location and physical/chemical properties, (2) the objectives to be met during the response, and (3) the nature and amount of resources (people and equipment) available.

It is important to recognize that the purpose of this paper is not to identify the optimum spill response option. The preceding comments emphasize the fact that the ultimate selection of offshore response techniques is a spill-specific process. Instead, a number of performance-oriented parameters have been used to compare the general utility of these techniques. These parameters include the rate at which oil can be accessed; the sensitivity of each response system to wind and sea conditions; the efficiency with which oil can be recovered, treated, or

burned; and the potential volume control rate based on overall system performance.

OBJECTIVES

The primary objective of this paper is to provide oil spill response planners with a comparative assessment of performance expectations involving mechanical cleanup, chemical dispersants, and in-situ burning. Performance is examined for each mode of response based on specific equipment operating characteristics, environmental conditions, and known (or anticipated) efficiencies of use. Areal coverage rates for a number of selected response systems are combined with efficiency and maximum "oil handling" rates (for a given film thickness) to determine a range of potential oil volume control rates. The objective is to present these control rates for all three response modes graphically so that the relative merits and utility of each system can be identified.

A secondary objective is to provide the reader with an approach through which other spill control procedures and/or efficiencies can be examined and compared. The graphic representation of volume control rates for different response systems provides a useful tool for the rapid assessment of time and costs in dealing with a given spill situation.

It is hoped that the information presented in this paper will help response planners in selecting the right type and amount of equipment for a given spill situation. By modifying the operational or performance input used in this analysis, one can generate similar operational plots for specific equipment packages. Such plots can be useful quick-reference tools when one is attempting to identify the most practical and efficient mix of people and equipment for a particular spill.

SELECTION OF RESPONSE SYSTEMS

Seven separate categories for response equipment have been selected within the three primary modes of response (mechanical cleanup, dispersants, and burning). These categories include three sizes of skimming systems within the cleanup mode; vessels, helicopters, and fixed-wing aircraft for dispersant application; and fire containment boom towed in a U-configuration for the burning mode.

Typical operating characteristics have been selected for each response system to facilitate performance comparisons later on. These operating characteristics include:

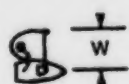
Swath Width	=	W
Speed	=	V
Throughput Efficiency	=	TE
Recovery Efficiency	=	RE
Burning Efficiency	=	BE
Dispersant Efficiency	=	DE
Maximum Pump Rate	=	MaxPR (for recovered fluids and dispersant application)

It should be recognized that the selected operational inputs reflect data for representative systems, not necessarily all equipment packages for that category. In most categories one can envision some device that has

operating characteristics that fall outside the range selected.

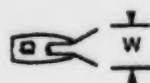
Mechanical Cleanup

Small Skimmers: Small self-propelled skimmers and portable over-the-side devices. Selected operating characteristics include:

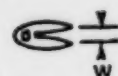


V = 0.25 to 0.75 knot
(0.5 to 1.4 kilometers/hour)

W = 6 to 25 feet (1.8 to 7.6 meters)



TE = 10% to 95% (discussed later in connection with Figure 3)



RE = 50% to 75%

MaxPR = 100 gallons/minute (379 liters/minute)

Medium Skimmers: Those moderately sized, self-propelled units or over-the-side skimming systems where small, towed diversion booms could be employed to extend the operating swaths. Selected operating characteristics include:



V = 0.5 to 1.0 knot
(0.93 to 1.85 kilometers/hour)

W = 50 to 100 feet (15.2 to 30.5 meters)

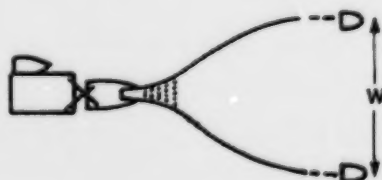
TE = 10% to 95% (discussed later in connection with Figure 3)



RE = 50% to 75%

MaxPR = 300 gallons/minute (1,136 liters/minute)

Large Skimmers: Relatively high-throughput units that would normally be used in conjunction with large V-boom configurations and auxiliary storage containers such as towed bladders or barges. Selected operating characteristics include:



V = 1 to 2 knots
(1.85 to 3.7 kilometers/hour)

W = 150 to 250 feet (47.5 to 76.2 meters)

TE = 10% to 95% (discussed later in connection with Figure 3)

RE = 50% to 75%

MaxPR = 600 gallons/minute
(2,271 liters/minute)

Chemical Dispersants

Vessel-Mounted Spray Systems: All dispersant application systems (large and small) that would be mounted on vessels. Selected operating characteristics include:



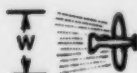
V = 5 to 10 knots (9.3 to 18.5 kilometers/hour)

W = 40 to 100 feet (12.2 to 30.5 meters)

DE = 20% to 70% (discussed later in connection with Figure 3)

MaxPR = 20 gallons/minute (75.7 liters/minute)

Small Fixed-Wing Aircraft and Helicopters: All dispersant systems that could be mounted on small fixed-wing aircraft and attached to or slung beneath helicopters. Selected operating characteristics include:



V = 40 to 80 knots (74 to 148 kilometers/hour)

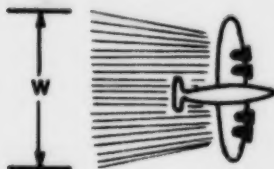
W = 40 to 80 feet (12.2 to 24.4 meters)



DE = 20% to 70% (discussed later in connection with Figure 3)

MaxPR = 120 gallons/minute (454 liters/minute)

Large Fixed-Wing Aircraft: All high-throughput dispersant spraying systems that could be wing-mounted or deployed from an aircraft cargo door (C-130) on large fixed-wing aircraft. Selected operating characteristics include:



V = 125 to 175 knots (232 to 324 kilometers/hour)

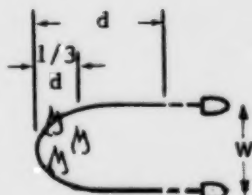
W = 100 to 200 feet (30.5 to 61 meters)

DE = 20% to 70% (discussed later in connection with Figure 3)

MaxPR = 900 gallons/minute
(3,400 liters/minute)

Burning

For comparison with other "moving" response systems, burning is envisioned here as oil which is trapped and burned at the apex of a towed fire containment boom in a U-configuration. Selected operating characteristics include:



V = 0.25 to 0.75 knot (0.5 to 1.4 kilometers/hour)

W = 150 to 300 feet (46 to 92 meters)

BE = 80% to 98% (discussed later in connection with Figure 3)

Oil and burn area restricted to $1/3 d$ (inset drawing at left)

Swath (W) = $0.3 \times \text{Boom Length (L)}$

L = 500 to 1,000 feet (152 to 305 meters)

Burn Rate = $0.023 \text{ to } 0.07 \text{ gallons/minute/foot}^2$
($0.94 \text{ to } 2.85 \text{ liters/minute/meter}^2$)

OIL ACCESS RATE FOR SELECTED RESPONSE SYSTEMS

The selection of a suitable response package, be it a mechanical, dispersant or burning system, will depend in part on the areal extent of the spill to be encountered. The expected areal coverage rate for a given system will strongly influence that unit's ability to access a significant portion of a spill within a reasonable time frame. Such rates of coverage, typically given in acres/minute (or hectares/minute), will help to identify the appropriate number and mix of response systems for a particular spill situation.

In the previous section, the selected operating characteristics were provided for each of the seven response systems used in this paper. The operating swath (W) and speed (V) characteristics can be used to determine the range of values for each system's areal coverage rate using the expression:

$$\text{Areal Coverage Rate (gallons/minute)} = W \text{ (feet)} \times V \text{ (knots)} / 430$$

The areal coverage rates are thus provided in Table 1 and in Figure 1.

TABLE 1 AREAL COVERAGE RATES FOR SELECTED RESPONSE SYSTEMS

SYSTEM	AREAL COVERAGE RATE	
	(acres/minute)	(hectares/minute)
MECHANICAL RECOVERY		
Small Skimmers	0.004 - 0.044	0.001 - 0.018
Medium Skimmers	0.058 - 0.233	0.023 - 0.094
Large Skimmers	0.349 - 1.163	0.141 - 0.471
DISPERSANTS		
Vessels	0.465 - 2.326	0.188 - 0.941
Sm. F.W. Aircraft/helo's	3.721 - 14.884	1.506 - 6.024
Lg. F.W. Aircraft	29.070 - 81.395	11.765 - 32.941
BURNING		
Fire Cont. Boom (U-config.)	0.087 - 0.523	0.035 - 0.212

As indicated, the areal coverage rates for these representative systems cover more than four orders of magnitude. The estimated rate at which oil can thus be accessed with a given system is definitely a significant consideration in the overall assessment of performance, particularly on large, widespread spills. Large skimming systems and vessels with dispersant spray units, for example, would normally access oil layers at a rate on the order of 1 acre/minute (less than 1/2 hectare/minute). It would therefore take such a unit at least 10.5 hours to access the oil from a 1-square-mile (2.59-square-kilometer) slick, without consideration for lost time due to turns, repositioning, equipment down-time, etc. Depending on the weather, the nature of the oil, the location of the spill with respect to land, etc., consideration of the access rate alone may be enough to rule out certain modes of response. Such consideration, on the other hand, may simply indicate the number of response units needed to access all or part of the spill.

ENVIRONMENTAL INFLUENCES ON SYSTEM PERFORMANCE

This section is not intended as a comprehensive assessment of the many ways in which environmental factors could help or hinder the various modes of responding to an offshore spill. A thorough treatment would have to at least include wind and waves, visibility, ice conditions, air and water temperatures, etc. Instead, it will be assumed that for comparison

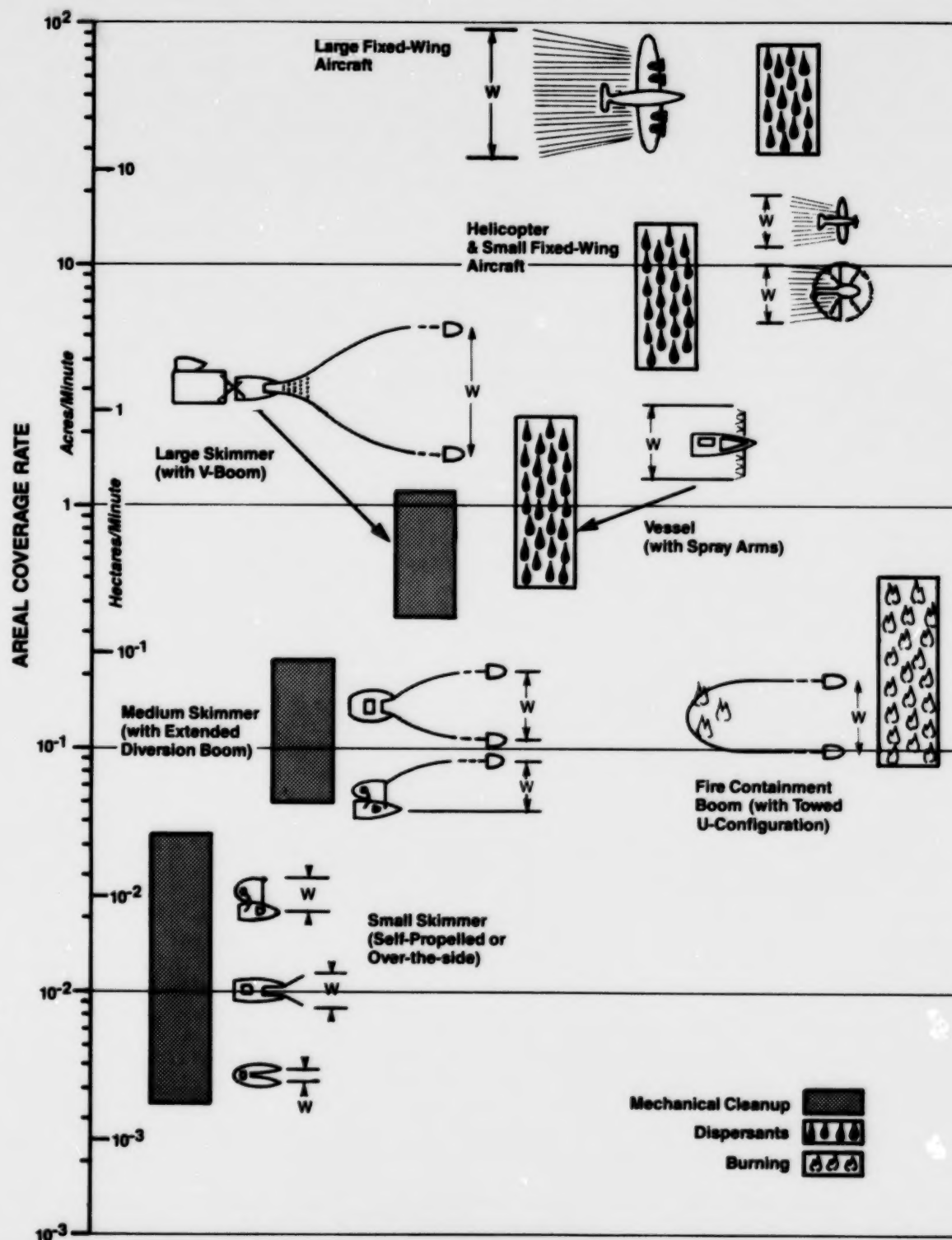


FIGURE 1: AREAL COVERAGE RATES FOR SELECTED SPILL RESPONSE SYSTEMS

purposes, each response technique would be dependent on reasonable visibility, relatively open-water conditions, and air and water temperatures that do not preclude the use of skimming, dispersing and burning techniques. It will further be assumed that the oil in its initial condition can be reasonably picked up, dispersed or burned.

With time, offshore slicks will quickly spread, weather, emulsify and disperse, thus altering the ease with which the above response options can be exercised. These natural processes will affect the oil's viscosity, thickness, water content, flammability, etc., and these variables will in turn affect the recoverability, dispersability, and burnability of the slick. The potential utility of a given response mode under various environmental conditions is further complicated by the type of pickup device (direct suction, weir, centrifugal, submersion or oleophilic), the type of dispersant to be used, and the type of oil spilled. The complexity of addressing all of these variables is beyond the scope and intent of this paper.

Several important observations can be made, however, with respect to some key environmental factors. Wind and sea conditions, for example, are very important because they influence not only equipment and personnel performance, but the movement and condition of the oil as well. Strong wind and wave conditions can quickly render booms and skimmers ineffective, reduce the accuracy of applying chemicals, cause oil to disperse naturally (thus reducing the need for dispersants), and prevent oil from being ignited and/or burned efficiently. The effects of wind and sea state, as well as many other environmental conditions, relate strongly to the changes in the thickness of a slick.

For these reasons, Figure 2 has been developed to show how mechanical cleanup, dispersing and burning techniques might be related to a range of oil film thicknesses and varying wind and sea conditions. It is understood that within a very short distance across any spill, the oil could easily have thicknesses ranging over several orders of magnitude. It is not uncommon to have dark blue-black oil layers or wind-blown streaks of oil a tenth of an inch (2 to 3 millimeters) in thickness surrounded by layers thinning down to rainbow-colored films a few hundred-thousandths of an inch in thickness. It is this variability in thickness that makes volume estimates so difficult, recovery systems often inefficient, and dispersant usage quite challenging from a dosage and efficiency standpoint.

The author has witnessed and worked on many hundreds of accidental and experimental oil spills over the past 20 years. Based on that experience and the available literature, it is the author's opinion that the following statements (some of which are reflected in Figure 2) are generally true:

- (1) Most spills (large and small) in an offshore environment (anything above a Beaufort Scale 1 under tropic/temperate conditions) will reach film "thinnesses" that are typically a few hundredths of an inch (about 1 millimeter) down to the barely perceptible sheens (millionths of an inch) in less time than it normally takes to be on scene with shore-based response equipment (say, 2 to 4 hours).
- (2) Under extreme cold-climate conditions, Item 1 above is generally true unless ice is present and/or seas are less than a Beaufort Scale 3, in which case major portions of a spill may remain at thicknesses on the order of a tenth of an inch (2 to 3 millimeters) for many hours to even days (in a calm, windless sea).

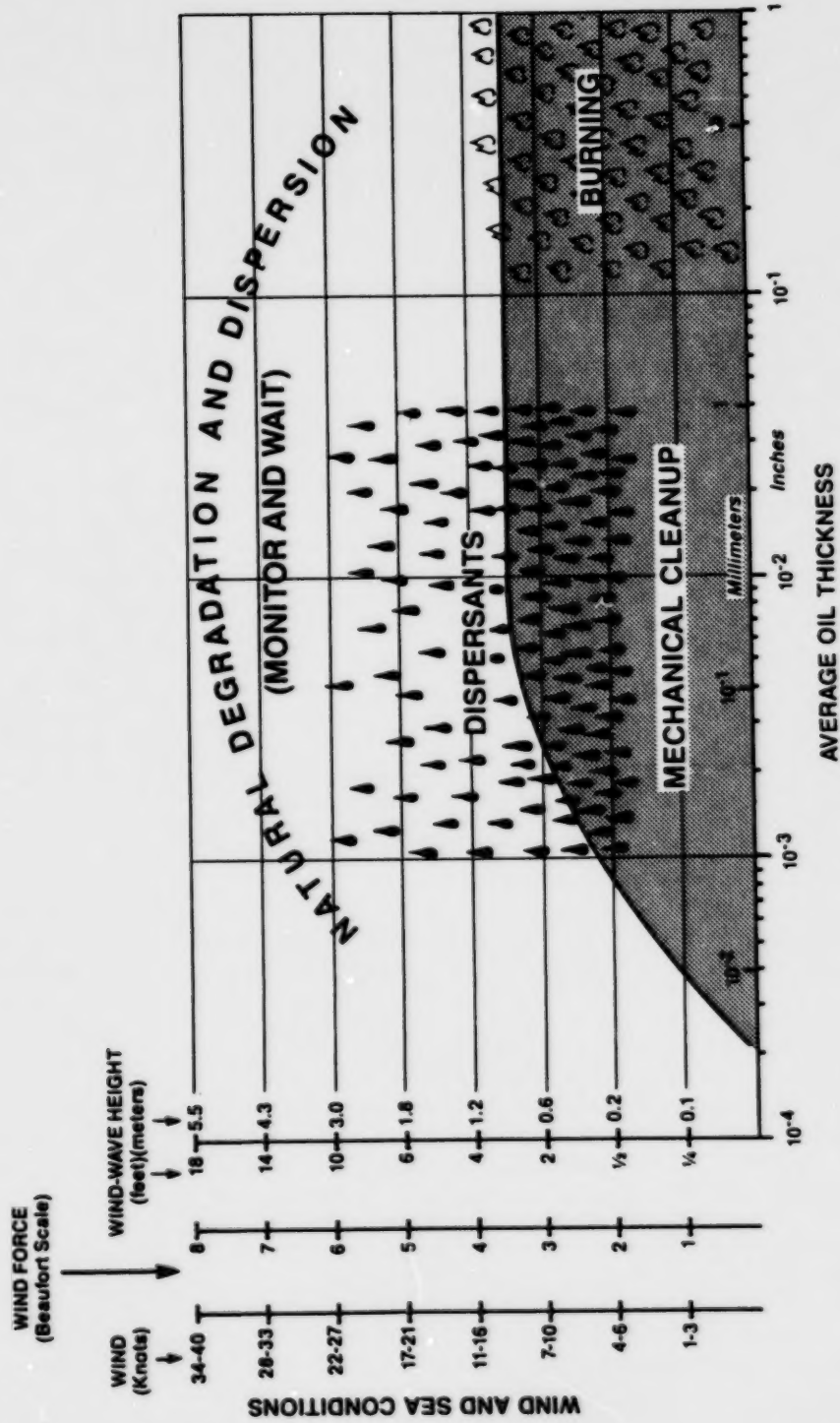


FIGURE 2: PRIMARY SPILL RESPONSE OPTIONS UNDER VARIOUS WIND/SEA CONDITIONS AND OIL FILM THICKNESSES

- (3) In light of the above, oil cannot normally be efficiently burned (except under calm, cold/ice conditions) without the aid of fire containment boom. Burning on water will require a minimum thickness of approximately a tenth of an inch (2 to 3 millimeters) and substantially thicker layers for sustained, efficient elimination of oil. It has also been observed that the ignition of most oils becomes difficult at wind speeds approaching 20 knots. Once ignited, however, such burns have been sustained with much stronger winds.
- (4) Mechanical cleanup techniques typically work best on thick oil layers with calm seas. The practicality of such techniques drops off quickly as film thicknesses drop below a thousandth of an inch (a few hundredths of a millimeter) and as wind/sea conditions move above a Beaufort Sea 3 to 4 condition. At thicknesses greater than a thousandth of an inch (10^{-3} inch), most oils retain their natural color -- for example, crude oil normally appears blue-black.
- (5) As short-period wind-waves build to about 2 to 3 feet (0.6 to 0.9 meters) or greater, most booms suffer significant losses due to entrainment and/or splashover. The horizontal portion of the mechanical cleanup envelope in Figure 2 could be raised to higher sea states for some high-seas skimming systems; however, the majority of recovery systems (particularly those depending upon booms for support) fall below the designated cleanup curve.
- (6) The lower end of the cleanup curve (at a thickness of about 2×10^{-4} -inch) is estimated as the general thickness regime where the volume per unit area (about 5 gallons/acre or 50 liters/hectare) would yield little if any reward with most skimmers.
- (7) The majority of controlled dispersant application work has been conducted on slicks that fall between a few thousandths of an inch (several tens of microns) to a few hundredths of an inch (several hundred microns). With some evidence that dispersion can be chemically induced at thicknesses less than and greater than this relatively narrow band, Figure 2 has been prepared with the upper and lower bounds currently set at 4×10^{-2} inch (1 millimeter) and 10^{-3} inch ($2\frac{1}{2}$ hundredths of a millimeter, or 25 microns).
- (8) The upper and lower bounds for wind/sea conditions with dispersants have been drawn at around Beaufort Scale 5 to 6 and at about Beaufort Scale 2, respectively. Dispersants could be applied under much stronger wind and sea conditions; however, it is debatable as to whether such chemical assistance would be necessary or cost-effective in a fully developed sea. At the lower end of the dispersant envelope, treatment and dispersion might be achieved with so-called "self-mixing" dispersants; however, there remain many questions regarding how much oil will remain dispersed and for how long under relatively calm conditions.
- (9) Natural degradation and dispersion (including evaporation) will, of course, continue to play an important role, regardless of the

response option(s) employed. The reliance on these processes under certain circumstances (sometimes referred to as the "Monitor and Wait" option) can be the safest, most cost-effective and environmentally-sound approach to an offshore spill. The only problem with waiting, however, is the risk that should an alternate response be subsequently needed, it may well be too late to use cleanup, dispersant and burning techniques efficiently. The next step may only be that of shoreline cleanup and restoration.

The points made above and the envelopes drawn in Figure 2 will undoubtedly stimulate some debate. However, these considerations will be used in the following section to develop yet another set of assumptions regarding response option efficiencies.

SYSTEM PERFORMANCE EFFICIENCIES

The same estimated average thickness boundaries provided earlier for each of the primary response categories have been used to develop Figure 3 as well. In Figure 3, however, an effort has been made to identify a reasonable range of efficiency values for the average thicknesses over which each response option could conceivably be used.

With respect to each of the response categories, rough-edged shading or symbols have been used to reflect the uncertainty of such efficiency estimates. In the case of mechanical cleanup, the suggested efficiencies of 30% to 60% at 10⁻³-inch thickness, of 50% to 80% at 10⁻²-inch thickness, etc. simply reflect approximate throughput efficiencies (TE) that the author has experienced with some skimming systems under comparable thickness regimes. A portion of the cleanup efficiency plot has been developed from experience with very efficient skimmers in the 90% to 95% range at thicknesses of several millimeters or more. With other, less effective systems, as much as 40% to 50% of the oil encountered passed right through the system. Had the diagram included thicker layers, it might be argued that the efficiency envelope should drop down again to reflect lower throughput efficiencies as discs, belts or mops become saturated or as a system's pumping capacity is reached. It was felt, however, that for the likely range of thicknesses to be encountered under most offshore conditions, the thickness range of Figure 3 should be sufficient.

The range of values and shape of the dispersant efficiency envelope are without a doubt the most arguable of this figure, if not this paper. Dozens of recent publications dealing with a variety of dispersant effectiveness tests and field trials have been examined; however, very little information exists on dispersant efficiency for various oils and dispersants over a range of carefully controlled thicknesses. Some of the studies referred to include: Brown et al., 1987; Swiss et al., 1987; Chau and Mackay, 1987; Belore, 1986; Mackay and Chau, 1986; Brown et al., 1985; Gill et al., 1985; and Nichols and Parker, 1985. Based on these and many other publications and recent discussions with dispersant researchers, the dispersant envelope of Figure 3 has been proposed as a "first cut" at what will hopefully become better defined through future research and sea trials.

The actual efficiency of dispersion is very difficult to define, let alone the assignment of values to it. Many researchers disagree on how, when, and where dispersant-treated oils should be sampled. There are uncertainties regarding the rate at which dispersants lose their

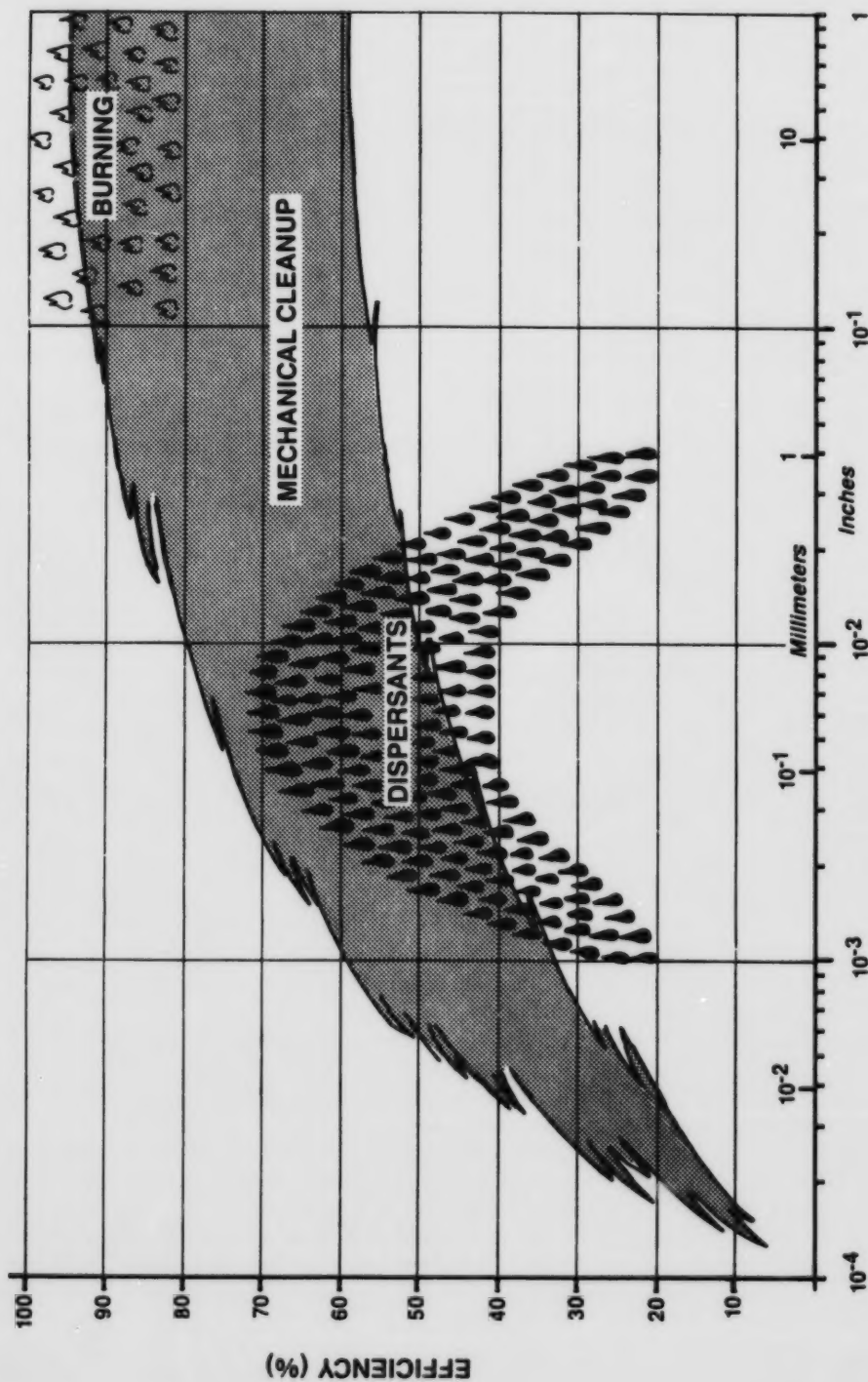


FIGURE 3: SELECTED PERFORMANCE EFFICIENCIES FOR PRIMARY RESPONSE TECHNIQUES OVER A RANGE OF OIL FILM THICKNESSES

effectiveness in maintaining a properly dispersed oil layer, and whether certain dosages (typically between 2 and 10 gallons/acre or 18 and 94 liters/hectare) should be modified to accommodate different types and thicknesses of oil. The overall volume of dispersant per unit area of oil slick will obviously vary (along with the resulting degree of dispersion) depending on the accuracy of overlap zones in single-pass operations and whether multiple-passes (on the same slick) are permitted.

It will be impossible to satisfy both the dedicated devotee for dispersant domain and the desperate desperado for dispersant demise! However, it is hoped that the dispersant efficiency envelope selected will serve as a reasonable approximation for the comparative performance calculations discussed in the following section.

The efficiencies selected for the in-situ burning portion of Figure 3 represent known data from a great many burns of oil on water in Canada and in the United States (Allen, 1987; Buist, 1987; Smith and Diaz, 1985; Shell et al., 1983; and Shell et al., 1984). With containment of a spill using fire containment boom, efficiencies of 95% to 98% can often be achieved under desirable burn conditions (i.e., relatively calm water with light to moderate winds). The range of efficiency has been shown as between 80% and 98% in Figure 3 to allow for the possible reduction in efficiency under more adverse conditions. As stated earlier, burning would be limited to thicknesses in excess of 10^{-1} inch (2 to 3 millimeters) and winds (for ignition) of approximately 15 to 20 knots or less. The actual efficiencies for combustion of spilled oil will depend on other factors such as the flammability of the oil upon ignition, the manner in which oil is actually fed to the burn area, the effectiveness of the boom in preventing entrainment and splashover during the burn, and the potential for re-igniting any burn residue with additional captures of oil.

POTENTIAL VOLUME CONTROL RATES

At this point, one can reach some rather obvious and important conclusions regarding the relative advantages and disadvantages of mechanical cleanup, dispersant, and burning techniques. Before doing so, however, there is an additional comparison that can be made by combining the areal coverage rates for each of the individual response systems (Figure 1) with the defined thickness-operating windows and efficiencies for each (Figures 2 and 3). The maximum pump rates (MaxPR) for recovered oil and water and the recovery efficiencies (RE) for each mechanical system are then included in the analysis to determine the estimated volume control rate (amount of oil picked up per unit of time) for each response system.

Similarly, the estimated volume control rate for dispersant application systems is determined using each spraying platform's areal coverage rate for a given thickness, efficiency of dispersion, and maximum dispersant pump rate (MaxPR). The estimated volume control rates thus achieved can then be compared with the theoretical maximum oil treatment rate for each application system. The theoretical maximum treatment rate is determined by combining the maximum dispersant pump rate with the expected (manufacturer's recommended) dispersant-to-oil ratio (DOR). In this analysis, DOR values between 1:20 and 1:50 were used and consistently found to result in theoretical treatment rates higher than the actual estimated control rates. The estimated volume control rate is considered a reasonable number if it is equal to or less than the theoretical maximum oil treatment rate.

It is also possible to estimate a volume control rate for burning by first determining the area of an oil layer that could normally be held within the boom configurations described earlier. Then, by combining the range of known burn rates (for thick and thin films), one can determine the rate at which oil could be eliminated from each contained area. These elimination rates are then reduced by the range of efficiencies established in Figure 3 to come up with the final estimated control rates for in-situ combustion using the boom lengths and widths described earlier.

The area of the contained oil layer for a given boom length is calculated based on containment within only that portion of the U-configuration that is less than one-third the distance from the curve of the boom to the leading ends of the "U" (Shell et al., 1984). The 500-foot (152-meter) and 1,000-foot (305-meter) boom lengths are assumed to have swath-width openings (W) of 150 feet (46 meters) and 300 feet (92 meters), respectively. Estimated oil areas of approximately 7,000 feet² and 27,000 feet² for the two boom configurations are then combined with known burn rates of from 0.023 gallons/minute/foot² to 0.07 gallons/minute/foot² to determine the theoretical elimination rates for each containment area. These numbers are then reduced by the efficiency estimates of Figure 3.

The methods described above for each of the seven selected mechanical cleanup, dispersant application, and burning systems were used to develop the information presented in Figure 4. This type of graphical comparison is based on actual oil access rates for representative recovery, chemical spraying, and burning systems currently available. The user of this diagram can make quick comparisons of the potential oil handling capacity (or volume control rate) for any of the seven systems described in this paper. It must be realized, however, that such control rates are based on the efficiencies described earlier. These rates of control are also intended as recovery or treatment rates when each system is actually "working". That is, one must make separate assessments of each system's requirements for mobilization and transit to a spill, time for turns/repositioning, time for refueling and for off-loading recovered oil and water (with recovery systems), down-time for maintenance, etc. Used properly, Figure 4 (or variations of it) can provide useful comparisons of equipment performance for spill response strategy planning, developing scenarios, and assessing equipment needs.

Referring to Figure 4 for example, one can see that dispersant spraying from fixed-wing aircraft and helicopters can have a "potential" tenfold to hundredfold increase in volume control rate over other spill response systems. This observation, however, must be viewed in light of the dispersant efficiencies described earlier, the range of oil thicknesses for effective use (which translate into dosage requirements as well), government approval requirements (which may result in missing a critical dispersant time window), etc. With vessel-mounted dispersant-spraying systems, the potential control rates fall in line with the larger mechanical cleanup systems. This is understandable even though the dispersant platforms may move five to ten times faster than the recovery systems. That is, the swaths and potential efficiencies of the skimmer and V-boom systems help make up for their slower speeds.

While comparing mechanical cleanup with dispersants, one can see in Figure 4 that dispersants and recovery systems generally become equally impractical at film thicknesses much below a thousandth of an inch (or a few hundredths of a millimeter). Such observations, of course, must again be weighed in light of other considerations. For example, it may well be

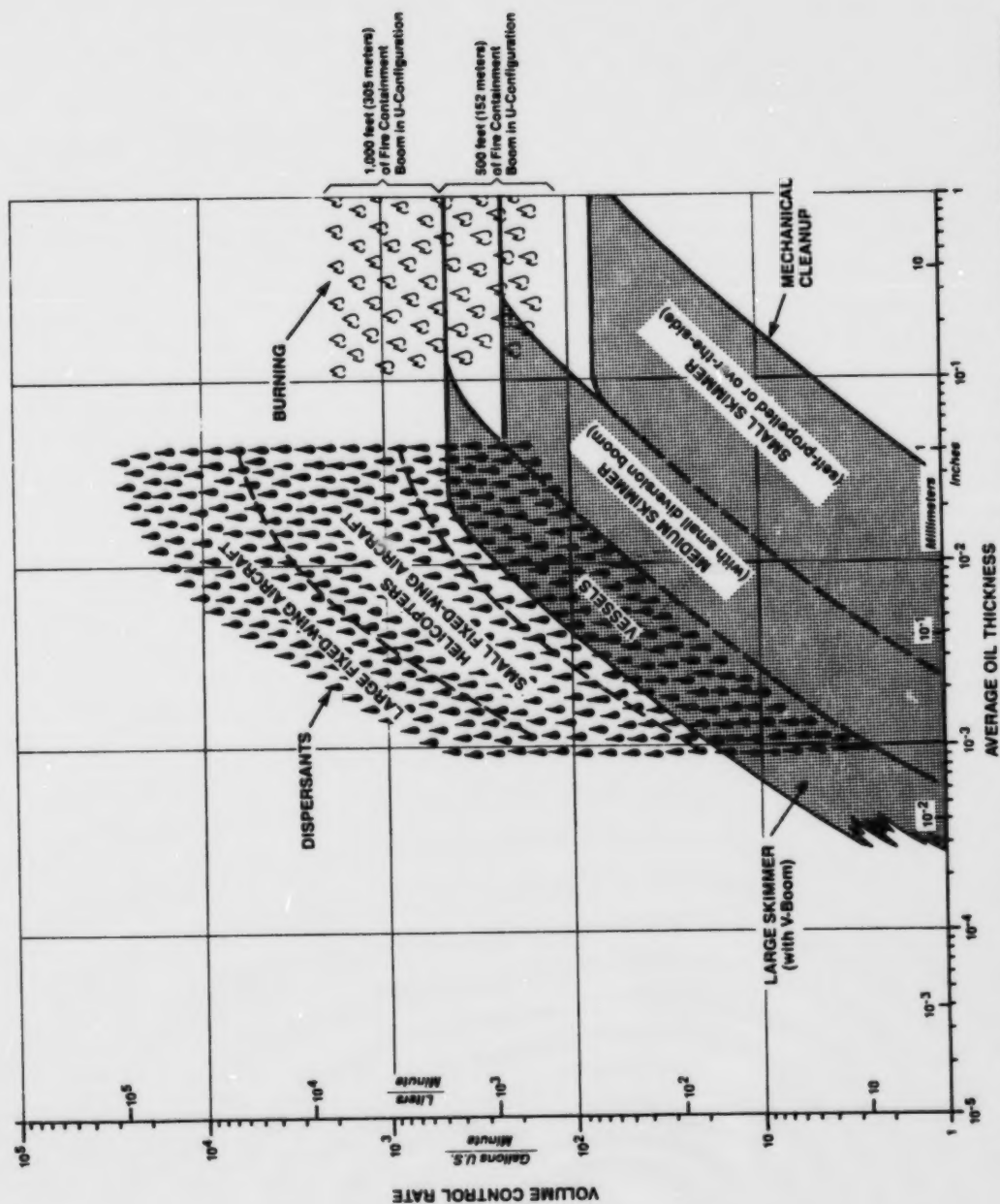


FIGURE 4: COMPARISON OF POTENTIAL VOLUME CONTROL RATES FOR SELECTED SPILL RESPONSE TECHNIQUES

prudent to operate one or more cleanup systems even inefficiently for awhile if they are not needed for higher priority work and if their minimal volume contribution still helps ease certain socio-political pressures.

At the upper end of the thickness range, all of the mechanical cleanup systems continue to function, as expected, while the dispersant response becomes inappropriate. At thicknesses greater than 1 millimeter, for example, a dispersant rated at even 1:50 for its DOR would need to be sprayed at dosages of 20 gallons/acre (187 liters/hectare) or more. At these thicknesses of a millimeter or more, it can be seen that many of the medium to large recovery systems selected are at or near their maximum volume control rates (the flat portion of their plots in Figure 4). These maximum recovery values depend upon the maximum pump rate for the system and the estimated recovery efficiency, RE (the percentage of oil contained in the total fluid picked up). Such systems would have to reduce their operating swaths and/or speeds to avoid excessive reductions in their throughput efficiencies at the greater thicknesses.

Regardless of the mechanical recovery systems selected in Figure 4, their typical volume control rates of tens to hundreds of gallons/minute (say 100 to 1,000 liters/minute) fall substantially below the hundreds to thousands of gallons/minute that might be eliminated with burning. With only one 1,000-foot (305-meter) length of fire containment boom in operation, in-situ combustion could eliminate up to 1,800 gallons of oil per minute. And, since the lower end of the boom could hold approximately 18,000 gallons of oil for each inch of oil depth, the established burn rates (on the order of a tenth of an inch per minute or 0.07 gallons/minute/square foot) suggest that the burning of the 18,000 gallons (about 68,000 liters) would actually take less than 10 minutes.

Again, the estimated volume control rates for burning must be interpreted in full light of the many constraints for an effective burn. The contained oil will be subjected to the same potential losses through entrainment and splashover that would occur with any other conventional boom. For burning to take place, the oil must still contain enough of its lighter flammable components, it must not be heavily emulsified, and an effective ignition source must be available to activate the burn. Recent field tests have demonstrated that a Helitorch releasing burning globules of gelled gasoline from a helicopter-slung unit (Allen, 1987) can effectively ignite floating oil under calm to moderate wind conditions.

SUMMARY STATEMENT

This paper has provided a summary of some of the most important operational considerations needed to assess the relative performance capabilities of offshore response systems available for mechanical cleanup, dispersant application, and in-situ burning. By defining ranges of values for possible areal coverage rates, efficiencies of use, pump rates, burn rates, etc., it has been possible to combine these data and to express them as potential volume control rates for each response system. Each of the above parameters has been evaluated wherever possible with respect to its dependence on average oil film thickness. The result has been the development of estimated performance plots that can be used to compare the three primary response modes under a range of environmental and film thickness conditions.

A careful assessment of the information presented in Figures 1 through 4, and a thorough review of the constraints related to each mode of response leads to the conclusion that no one response system can handle the variety of conditions normally encountered in an offshore spill. Not only is one response system insufficient, it is becoming increasingly clear that no one response mode is enough. Without a doubt, mechanical cleanup is still the only true "cleanup" technique -- dispersants and burning are simply response modes that serve to accelerate other natural processes (e.g., dispersion, degradation and oxidation). However, while dispersant application and burning techniques do not represent oil spill recovery modes, they do provide important backup capabilities in rounding out any organization's overall preparedness for an offshore spill. As is evident from the preceding figures and discussions, there can be times when mechanical systems may not be available, safe to operate, or simply enough to handle the entire spill. In such cases, dispersants and/or burning may be the only means of handling a spill or at least supplementing the efforts to recover oil.

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Hindcast of the Amoco Cadiz Oil Spill

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ABSTRACT

A coastal zone oil spill model developed for the U.S. Department of Interior, Minerals Management Service, was used to hindcast the fate of oil from the Amoco Cadiz tanker accident. Hindcasts were performed on two spatial scales, one small, to provide higher resolution of the coastline details within a few tens of kilometers of the wreck, the second extending several hundreds of kilometers along the coast. The mass balance and physical distribution of oil agreed reasonably well with area-wide observations for both large and small tests. Agreement at the larger scale deteriorated somewhat with respect to detailed spatial distributions. The small scale hindcast appeared to retain too much oil early in the simulation, although mass balances after 30 days agreed well with observations.

INTRODUCTION

Oil spill trajectory and fates models typically follow a surface slick until it contacts a coastline, at which time the simulation ceases. The model described here is designed to simulate oil spill fates both before and after a coastal contact.

Two statistical regression models have been developed previously to attempt to correlate length of coastline affected with oil spill size (Ford, 1985; Seip et al, 1986). By converting to log-log space, Ford (1985) was able to explain about 65% of the total variance in coastline affected using latitude and volume as the independent variables. The percent explained would presumably be considerably reduced in linear regression. Seip et al (1986) found no correlation between shore length damaged and the amount of oil spilled. Results of these efforts show the statistical approach to be relatively unsatisfactory for this problem.

Seip et al (1986) have also constructed a highly parameterized computational model for estimating length of shoreline affected following an oil spill. The model uses the amount of oil nearshore, littoral area, and a wave parameter (i.e. rough or smooth) as the primary input parameters. Removal of oil from the shoreline, or the water surface (via evaporation, entrainment, and advection out of the study area) are included as a single first order decay processes. Seip et al include no physical or chemical processes, except as represented by generalized input parameters. Therefore, the model cannot account for tides, complex topographical changes, wind direction and shifts, wave diffraction/refraction, longshore transport, effect of changing oil viscosity, compression of oil slicks against the shoreline,

and so forth. Although the model may be of limited use in some specific situations, it may prove useful in the more general applications of oil spill contingency planning, for which it was developed.

The coastal zone oil spill (COZOIL) model developed here has been designed to include explicit representations of as many of the known active processes as possible. Multiple discrete batches of oil, or spillets, are used to represent the surface slick. Spillets are circular while offshore but become elliptical upon contact with the shoreline. The amount of onshore-offshore foreshortening is governed by a balance between wind stress and gravity spreading forces, and results in alongshore spreading of the spillet. Evaporated hydrocarbons are given no spatial representation, but are simply accumulated from all sources during the simulation. Entrained oil offshore is represented by discrete particles which are advected by the local currents. Inside the surf zone, entrained oil takes on a continuous representation, discretized by alongshore grid cell. Transport in the surf zone is governed by a classical radiation stress formulation. Incorporation of water into surface oil (emulsification) is simulated offshore. De-emulsification (de-watering) is allowed to occur for oil which is on the foreshore or backshore.

Oil coming ashore may be deposited on the foreshore or the backshore, or carried into coastal lagoons, ponds, or fjords. Oil on the foreshore penetrates into the underlying sediments at a rate dependent on sediment grain size and oil viscosity. Oil may also be carried into the beach groundwater system by wave overwash. Reflotation of surface oil occurs during rising tides. These mass transfer pathways are shown schematically in Figure 1.

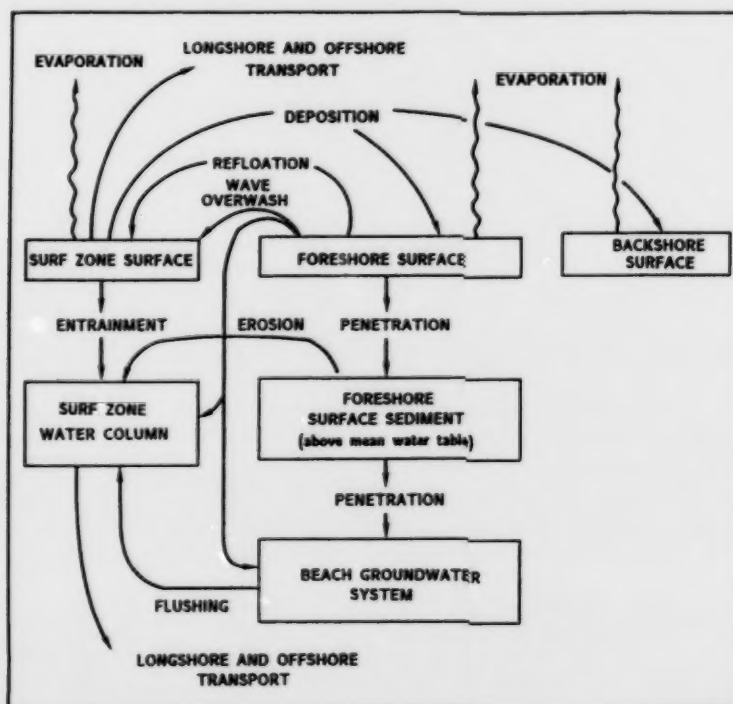


Figure 1. Schematic of processes included in the COZOIL model.

The most severe test of any model is a hindcast of a real event having a strong observational data base. The Amoco Cadiz spill offers the most complete data set of any coastal oil spill to date and, therefore, was selected to test COZOIL. Principal summary references on the spill are Hess (1978), CNEXO (1981), and NOAA/CNEXO (1982). Primary references concerning development of the COZOIL model are Gundlach and Reed (1986), Kana (1986), and Reed et al (1986, 1988).

The sequence of events to be hindcast began at 06:00 on 17 March 1978 when the supertanker began to break apart 2.4 km off the Brittany (France) coastline after grounding during storm conditions (Hess, 1978). A location map of the site is provided in Figure 2. The ship's cargo consisted of about 220,000 mtons of light Middle Eastern crude oil and a small amount of bunker oil, all of which was lost over the next two weeks (Hess, 1978). The oil rapidly emulsified in the high waves around the vessel, incorporating up to 90% water (Hann et al, 1978). After initial oil transport to the south, strong winds spread the oil towards the east for the first ten days. A shift in wind direction to the northeast then carried oil offshore, with a reversal toward the southwest after six days (Hess, 1978). Oil was ultimately spread over more than 300 km of coastline and a large area of offshore waters (Fig. 2).

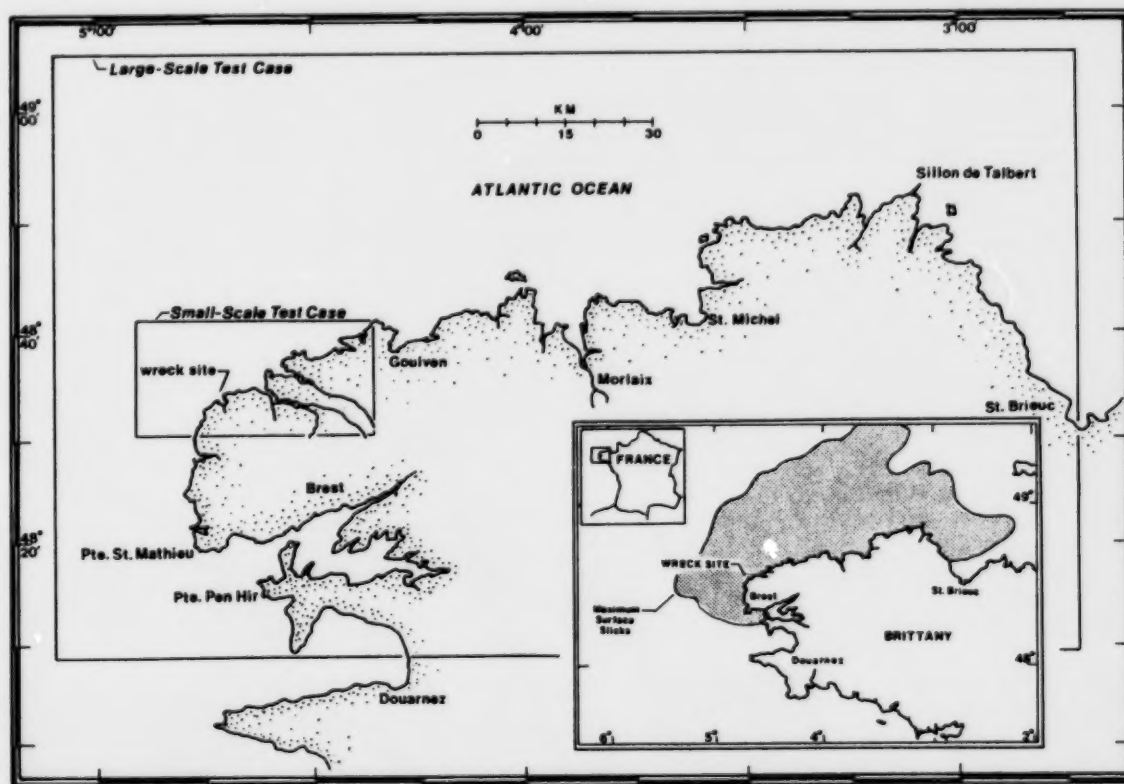


Figure 2. Study area map for the Amoco Cadiz hindcast showing coastal areas impacted by oil and borders of the small-scale and large-scale test cases.

MODEL INPUT DATA

The inputs to COZOIL used for the Amoco Cadiz test cases are presented in Table 1. Other inputs, such as simulation duration and time intervals between subsequent output to the monitor or data files are also required, but do not materially affect the computations.

The COZOIL model contains a library with seven crude oils and petroleum products. Of these, Murban Abu Dhabi appears to closely approximate the oil carried by the Amoco Cadiz (Anonymous, 1973; NOAA/CNEXO, 1982). The modeled release rate of oil is shown in Figure 3.

Air temperature for March and April 1978, as measured at the Brest airport, averaged about 7.5°C (Fig. 4). The wind time series used in the hindcast (Fig. 4) is also from Brest airport.

Hindcasts of the fate of the spilled oil were performed on small and large scales (Fig. 2) to reflect localized oiling within the convoluted coastline adjacent to the grounding site and to cover distribution over the entire spill-affected area. The Brittany shoreline being represented in the COZOIL model is complex and diverse, containing a closely spaced mixture of bedrock-dominated shores, mixed sand and gravel beaches, sand beaches backed by dunes or riprap, and estuaries with large mud flats. Because of the large tidal range, sand flats extending up to several kilometers from shore are exposed at low tide.

Table 1. COZOIL input parameters for deterministic simulation and values used for the Amoco Cadiz hindcasts

Input Parameters	Value	Comments
Oil type	Murban crude	Primarily light Arabian crudes (Hess, 1978)
Spill size	220,000 mtons	1,613,000 bbl (Hess, 1978)
Number of spillets	144	conforms to Hann et al (1978), Fig. 3.
Interval between sequential releases	1 every 2 hrs	conforms to Hann et al (1978), Fig. 3.
Coastal reach parameters	Reed et al, 1988	some field measurements
Air temperature	7.5°C	Brest airport, Fig. 4.
Wind time series	Fig. 4	Brest airport
Tidal period	12.4 hour	SHOM (1973, 1978)
Range	6.5 m	SHOM (1973, 1978)
Tidal current amplitude	1.46 m/sec	SHOM (1973, 1978)
Time after mean low tide for simulation start	6 hr	SHOM (1978)

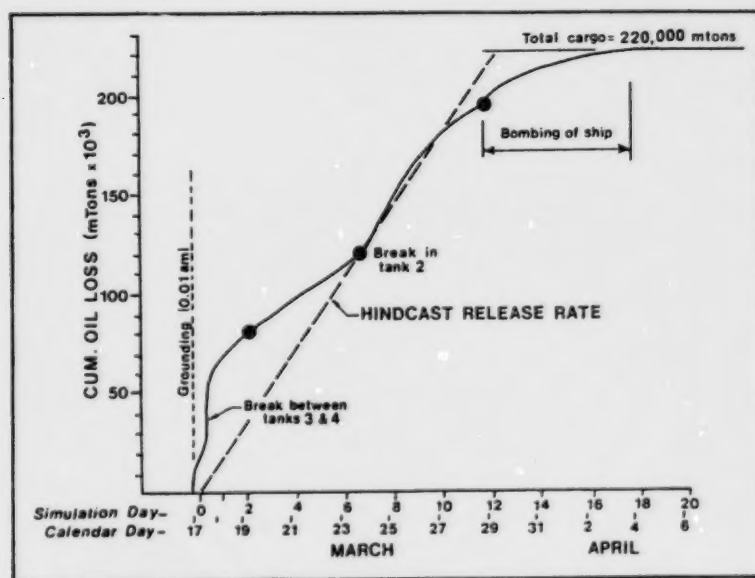


Figure 3. Estimated cumulative release of oil from the Amoco Cadiz. The solid line is from Hann et al (1978). The dashed line is the release rate used in the model hindcast.

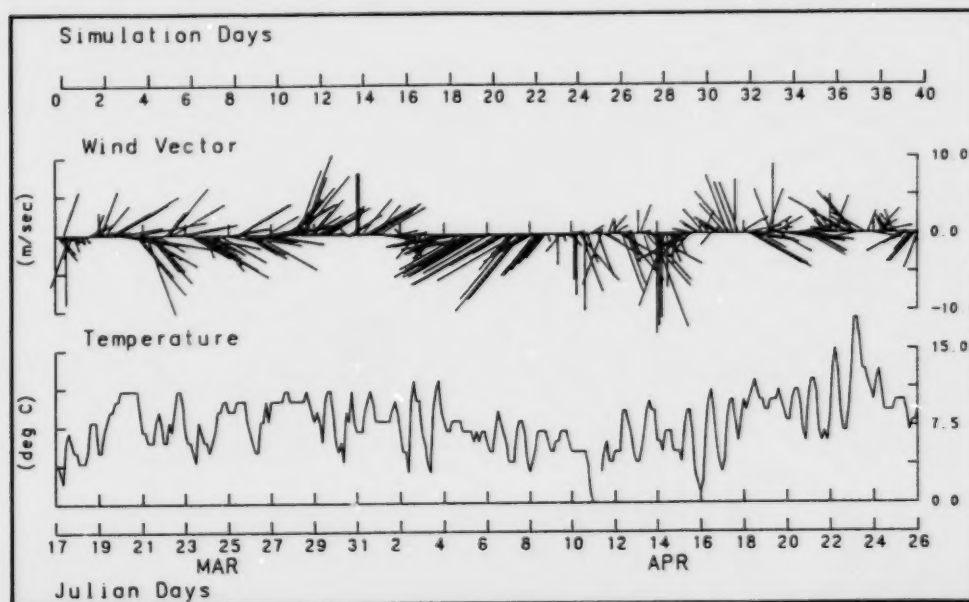


Figure 4. Temperature ($^{\circ}\text{C}$) and wind velocity (m/sec) from Brest airport for the major portion of the Amoco Cadiz spill duration (17 March - 26 April 1978).

Shoreline classification is based on Berne (1982), modified to conform with shoreline types defined by the COZIL model. Shoreline slopes are based on the measurement of topographic profiles across sand, coarse sand with fine gravel, and gravel beaches in Brittany at the time of the spill. Values for adjacent beaches were estimated using these measurements as a basis and from repeated observations of the shoreline by the second author. The foreshore slope, as defined by model requirements, is the slope of a straight line between the berm or high-water mark and the low-tide line. The backshore is the area above the berm or high-water mark. The position of this dividing line can vary substantially in Brittany depending on the tidal phase. A value of 20 m is used as representative of the narrow backshores common in Brittany.

The resulting coastlines for the two hindcasts are shown in Figure 5. In the small-scale case, lengths of individual shoreline segments or reaches vary from about 1.7 to 5 km. At this scale, the model is capable of resolving individual estuaries and embayments along the coast. For example, the Abers Benoit and Vrach (Fig. 5 top) are clearly represented. For the large-scale test case (Fig. 5 lower), the reach lengths range from 20 to 46 km, a much coarser representation in which 11 reaches cover over 600 km of actual coastline.

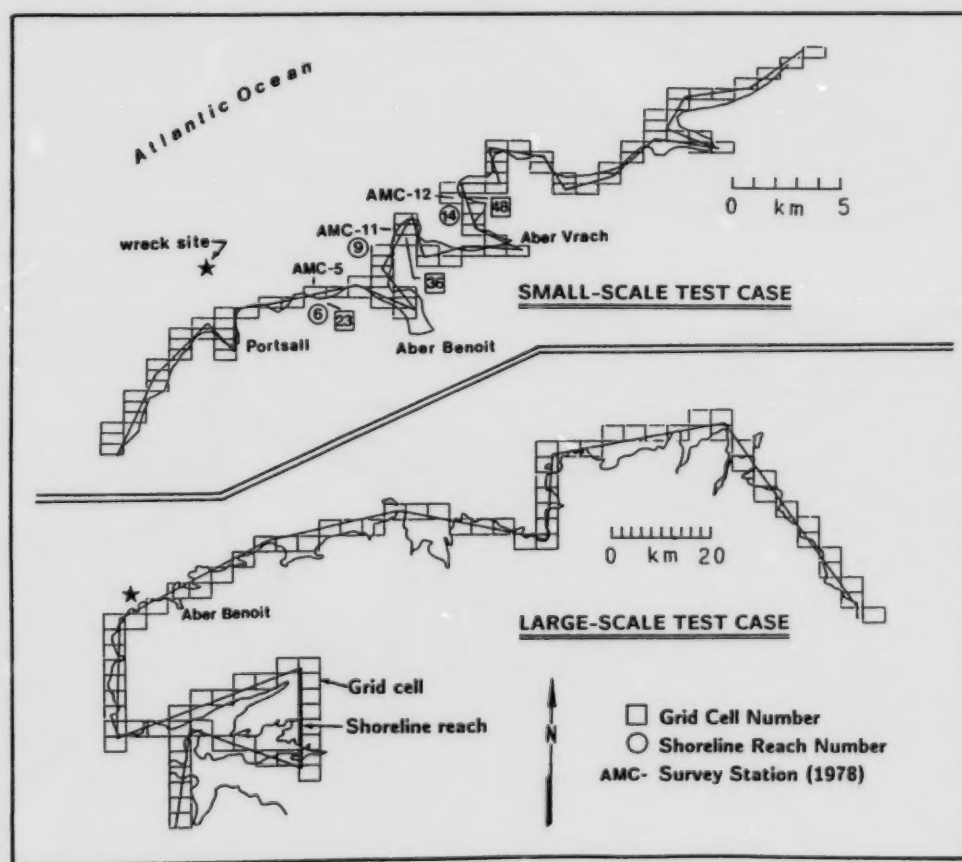


Figure 5. Modeled coastline for both test cases. Grid cells and shoreline reaches are indicated for each. The locations of field stations AMC-5, 11, and 12, are indicated in the top diagram.

SUMMARY OF OIL DISTRIBUTION DATA

The distribution and quantity of oil along the shoreline during the Amoco Cadiz spill was based on surveys conducted by a combined French-American field team. Measurements during the spill included oil thickness, surface coverage, burial, and alongshore distribution at twenty stations along the coast, augmented by approximately 150 additional ground observation stations and an extensive set of oblique and vertical aerial photographs. Results, published in Gundlach and Hayes (1978), D'Ozouville et al (1981), and Finkelstein and Gundlach (1981), indicate that approximately 62,000 mtons of oil were onshore during the period of 17 March to 2 April, and that from 20-28 April slightly less than 10,000 mtons was onshore.

For these simulations, original data were analyzed and recalculated to determine more exact dates with respect to onshore oiling, to differentiate between surface and buried oil, and to calculate 95% confidence intervals for each time period. Stations within the small-scale shoreline section were most often surveyed and provide oil quantities for three time periods, 8.5, 15 and 36 days after the beginning of the spill. For the large scale test, shoreline oil was calculated for 9 and 38.5 days after the initial release of oil. In all cases, the extent of shoreline oiling (in km) was taken from Finkelstein and Gundlach (1981) and D'Ozouville et al (1978). Only oiling of the mainland was considered as offshore islands and rocks are not represented in these model test cases.

RESULTS

The first simulation discussed is the small-scale test case, extending about 30 km from the spill site. The second is an order of magnitude more extensive spatially, representing over 600 km of actual coastline.

Small-Scale Test Case

For this test case, shoreline reaches vary from 1.7 to 5 km in length adjacent to the wreck site. The offshore model boundary is located 15 km or less from the shoreline (Fig. 2).

Offshore and onshore distribution

The distribution of oil on the water surface and on the shoreline for the small-scale test case is presented for four time periods in Figure 6. At 5 days, oil has already been distributed over the entire study area (onshore and offshore), conforming well to that reported by study of aerial photographs (CNEXO et al, 1978). This rapid distribution is the result of strong tides and winds, plus longshore transport inside the surf zone. At day 5, the model shows the highest surface oil concentration in Aber Benoit, an area that was heavily impacted by the spill and contained traces of oil at least until 1987. By day 10, oil quantity within Aber Benoit has decreased while oil in the nearshore area remains fairly evenly distributed alongshore but with less occurring along the eastern edge. Between days 10 and 20, most of the oil on the water surface has been transported out the northern model boundary due to strong offshore winds. A subsequent wind to the southwest, beginning about day 18, carries most of the remaining surface oil out the western model boundary. The overall sequence of oil distribution conforms very well to observations except that the actual spill contained no artificial boundaries so that re-oiling of the shoreline and offshore waters to the southwest occurred after transport offshore.

The onshore distribution of oil (Fig. 6) is represented by circles proportional to the total mass of oil found on the foreshore surface of the beach and the backshore of each grid cell. On day five, shoreline oil is concentrated in Portsall harbor adjacent to the wreck site, in Abers Benoit and Vrach, and on the two north-trending headlands (Presqu'île Ste. Marguerite and St. Cava) which form a barrier to the easterly drifting oil. This conforms very well with observations made at the time of the spill (Fig. 7).

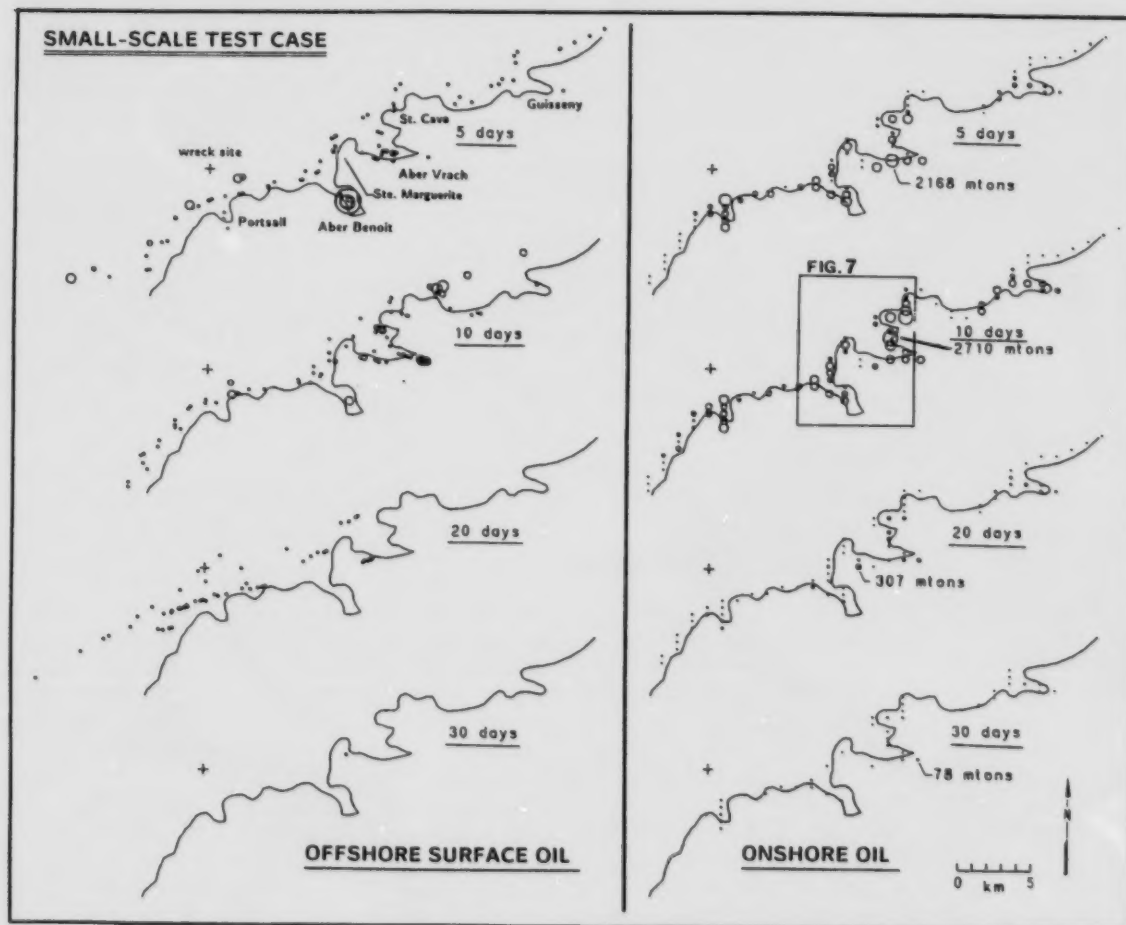


Figure 6. Distribution of offshore surface oil and onshore oil (foreshore surface and backshore) for the small-scale test case. Offshore, circles indicate computed areal coverage of thick oil. Onshore, circles are proportional to the oil mass associated with each grid cell. The maximum value of the circle for each time plot is given.

At day 10, the model indicates substantial oiling of the embayment at Guisseny as did occur; however, the model may over estimate oiling at this location because of the lack of shoreline detail. In this case, a large spit protecting the embayment is not adequately represented (Fig. 5 top). At days 20 and 30, oil is found along most of the coast in continually decreasing quantities.

The maximum amount of oil within any one cell equals 2710 mtons and occurs at day 10, corresponding to about 2 mtons of oil per linear meter of coastline. This maximum occurs on reach number 14, a sand beach, at a tidal height of 4.5 m. If the oil is evenly distributed over the exposed foreshore and backshore then the reach parameters indicate an areal coverage of about 15 kg/m^2 , or about 1.7 cm thick, considering that the oil has a density of approximately 0.9 g/cm^3 . This is the maximum oil holding capacity the model will allow for a sand beach (Gundlach and Reed, 1986; Gundlach, 1987). Thus oil arriving subsequently along this coastal cell on the water surface will be precluded from deposition until the tide drops, exposing more beach face, or oil on the beach surface is removed to the surf zone or penetrates into surface sediments.



Figure 7. Diagram indicating the observed distribution of Amoco Cadiz oil during late March from west of Aber Benoit to north of St. Cava. Compare to Figure 6, onshore oil distribution at 10 days. Arrowheads and dots indicate 1978 field stations (from Gundlach and Hayes, 1978).

Dynamic mass balances

The dynamic mass balance of oil for 40 days of simulation time is shown in Figure 8 for the small-scale study area. The bottom diagram shows the overall mass balance of oil divided into five major spill components: ashore, water surface, atmosphere, water column, and outside the simulation area. The curve labeled "Ashore" corresponds to the curve labeled "Total Ashore" of the middle diagram, which is composed of four subdivisions: foreshore, backshore, ground water, and surf zone. The top diagram of Figure 8 represents the total oil on the beach, composed of surface and backshore oil but excluding oil in the ground water. This represents the quantity of oil that would be measured on the beaches at the time of the spill. Estimated amounts of oil along this section of shoreline during the spill, compiled for 8.5, 15 and 36 days after the spill, are superimposed on this plot.

Figure 8 illustrates that the proximity of the release point to shore, combined with the onshore winds (Fig. 4) result in a steadily increasing amount of oil deposited onshore during the first 10 days. The removal and deposition of oil in conjunction with the rising and falling of the tide is clearly reflected in the interchange of oil between the ashore and water surface components. From days 10 to 15, the abrupt increase in oil mass leaving the study area, shown by the curve labeled "outside", is due to strong offshore winds. Note the simultaneous decrease in oil on the water surface (Fig. 8 bottom).

In comparing the observed versus simulated total quantity of oil ashore (Fig. 8 top), simulation values exceed observed values on both days 8.5 and 15, but compare well with those from day 36. Observations in the field were always made within low- to mid-tide levels, which conform to the higher values of total oil on the beach surface. The high oil quantities simulated on the shoreline could be due in part to removal rates which are too slow in the model and/or the absence of storm surge events in the hindcast. Two such events were recorded during the first two weeks following the start of the spill (Hess, 1978) and resulted in the rapid removal and transport of oil from several segments of the shoreline. The model, however, clearly shows dynamic variability both from low to high tide and from one tidal cycle to the next, which is entirely consistent with the field observations (Gundlach and Hayes, 1978).

Additional sources of error lie in the hydrodynamics incorporated into the model. As indicated in Figure 6, much of the onshore oil in the small-scale hindcast is associated with estuaries and embayments (Portsall, Aber Benoit, Aber Vrach, and Guisseny). Although most were indeed heavily polluted, the natural cleansing of these areas by tides is not represented in the simple hydrodynamics incorporated in the model. Finally, the hindcast does not include oil removed during cleanup, but this is thought to account for less than 20% of the oil ashore and did not reach maximum operation until two weeks into the spill (Hann et al, 1978).

Grid cell analysis

To view model predictions in further detail, oil distribution within three grid cells and their respective beach segments, were analyzed with respect to field site information. The locations of the shoreline reach, grid cells, and field stations, are presented in Figure 5 top. Plots of simulated and observed oil quantity, in mtons/km, for each of the three areas are presented in Figure 9. The individual grid cells, in particular, show large fluctuations in the amount of oil onshore, reflecting oil impacts followed by

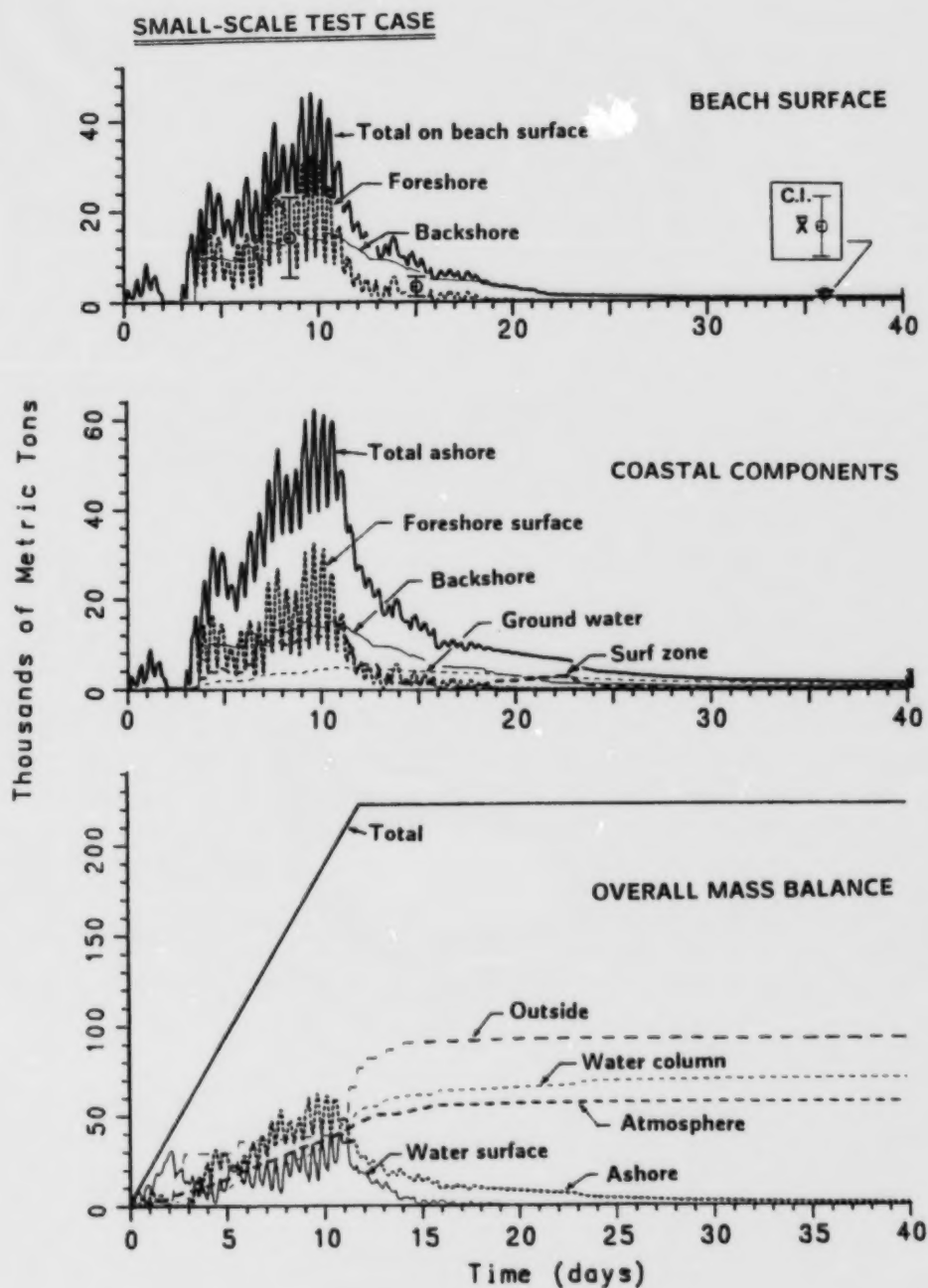


Figure 8. Dynamic mass balances (overall, coastal components, and beach surface) for oil associated with the small-scale test case. Observed values of oil quantity on the shoreline and 95% confidence intervals are indicated in the top diagram.

removal and transport to adjacent cells. Substantially less variability is evidenced when shoreline reaches (composed of 4 to 5 grid cells) are considered. This again corresponds to observations at the Amoco Cadiz spill site where it was common during the first two weeks to have very large oil concentrations at one beach while the adjacent beach escaped oiling entirely. The large increases in oil within the shoreline grid cell, as for stations AMC-11 (at days 5 and 10) and AMC-12 (at days 9 and 12) correspond to these large impacts. In these plots, the field value of oil quantity at AMC-5 is higher than that simulated, but comes close to the quantity noted less than two days later. The other two stations, AMC-11 and AMC-12, have observed oil quantities that are lower than the simulation values for shoreline reach, but are similar to those for the single grid cell.

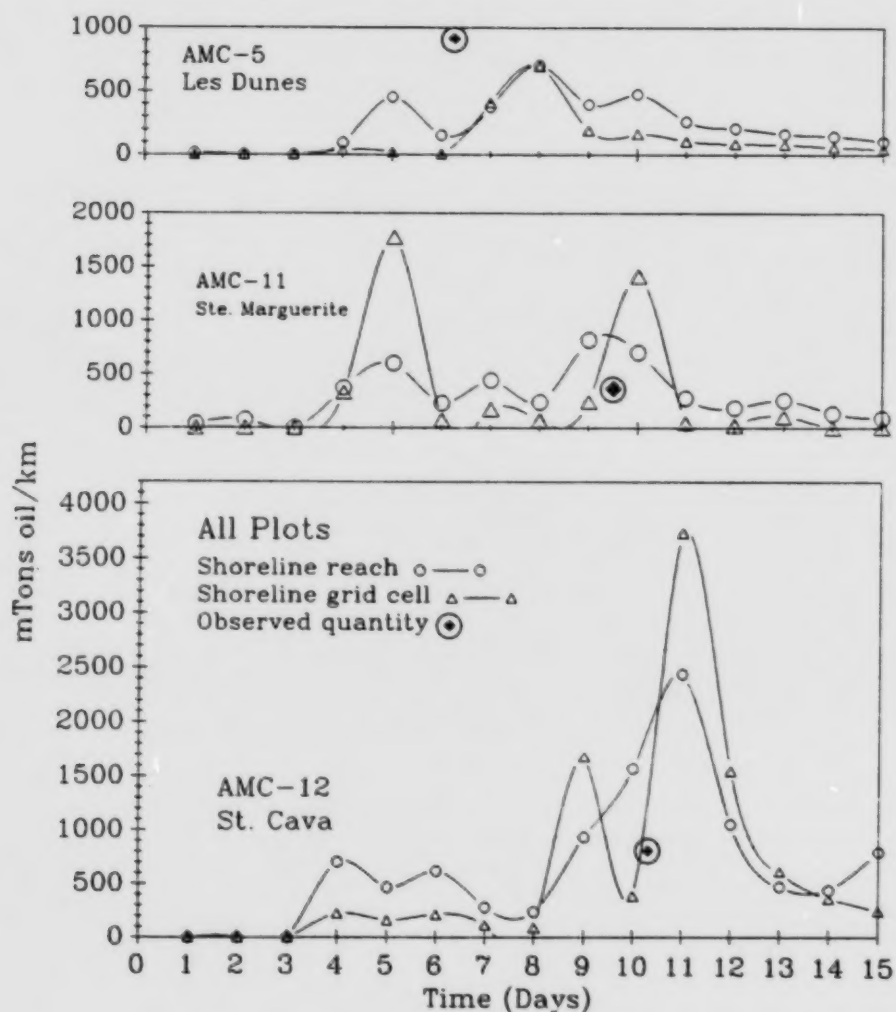


Figure 9. Comparison of oil quantity within individual grid cells and for the associated shoreline reach (composed of 4 to 5 grid cells) during the first 15 days of the oil spill. Values measured at field stations within the grid cell are indicated.

Large-Scale Test Case

This case encompasses the entire northwestern Brittany region and contains only 11 coastal segments ranging in length from 20 to 46 km in contrast to the previous case having a maximum length of 5 km (see Fig. 5). At this scale only coastline trends and very large embayments, as at Brest, can be differentiated.

Offshore and onshore distribution

Results of the large-scale simulation of the distribution of the oil is indicated in Figure 10. The distribution of offshore surface oil after 5 days compares extremely well with that observed after 4.5 days using vertical aerial photographs taken by the French government (CNEXO, et al, 1978) during the spill (Fig. 10, top left). The onshore distribution at this time also conforms very well that reported. Note the oiling at St. Michel, the site of a large kill of intertidal organisms (Hess, 1978). The consistent distribution for both the onshore and offshore cases continues through 10 days. Note particularly the oil along the shoreline from St. Michel to Ile Grande. Ile Grande was the site of extremely heavy concentrations within a marsh environment (Hess, 1978).

Between days 10 and 20, much of the onshore and nearshore oil is transported offshore because of the wind shift, and at day 20 the oil is returning from its northern excursion and poised to come onshore again. At day 30, this oil is transported to the southwest, oiling the shoreline south of the wreck site. This sequence of offshore transport with very late oiling of the shoreline to the south of the wreck site was well documented at the time of the spill (Gundlach and Hayes, 1978). The southernmost extent of shoreline oiling is essentially correct, ending at Pointe de St. Mathieu, although the model does have one impact near Pointe de Pen Hir which is not documented. The model, however, inadequately depicts the eastward transport of oil to Sillon de Talbert (Fig. 10), perhaps due to under estimation of tidal currents for this portion of the study area.

Dynamic mass balances

The various mass balances for the large-scale hindcast are shown in Figure 11. The effect of the extended boundary is immediately apparent when comparing this overall mass balance to that from the small-scale analysis (Fig. 8). The total lost out the model boundaries reduces from 30% after 15 days in the small-scale study to about 15% after 30 days in the large-scale test. Oil is transported north during the southerly wind event from days 10 to 15, but remains within the model boundaries. When the wind shifts back towards the southwest between days 16 and 21, some of the surface oil which was transported offshore comes ashore between days 22 and 29. Note the increase in the oil ashore at this time, particularly in plots of the coastal components and beach surface.

The total oil ashore is approximately the same (62,000-64,000 mtons) for the large- and small-scale test cases for the first 20 days. This is because the wind is almost continuously onshore for the first 10 days, then offshore for 5 days, and onshore again. The amount of oil on the beach surface, however, now agrees reasonably well with the field values after 9 days and 38.5 days.

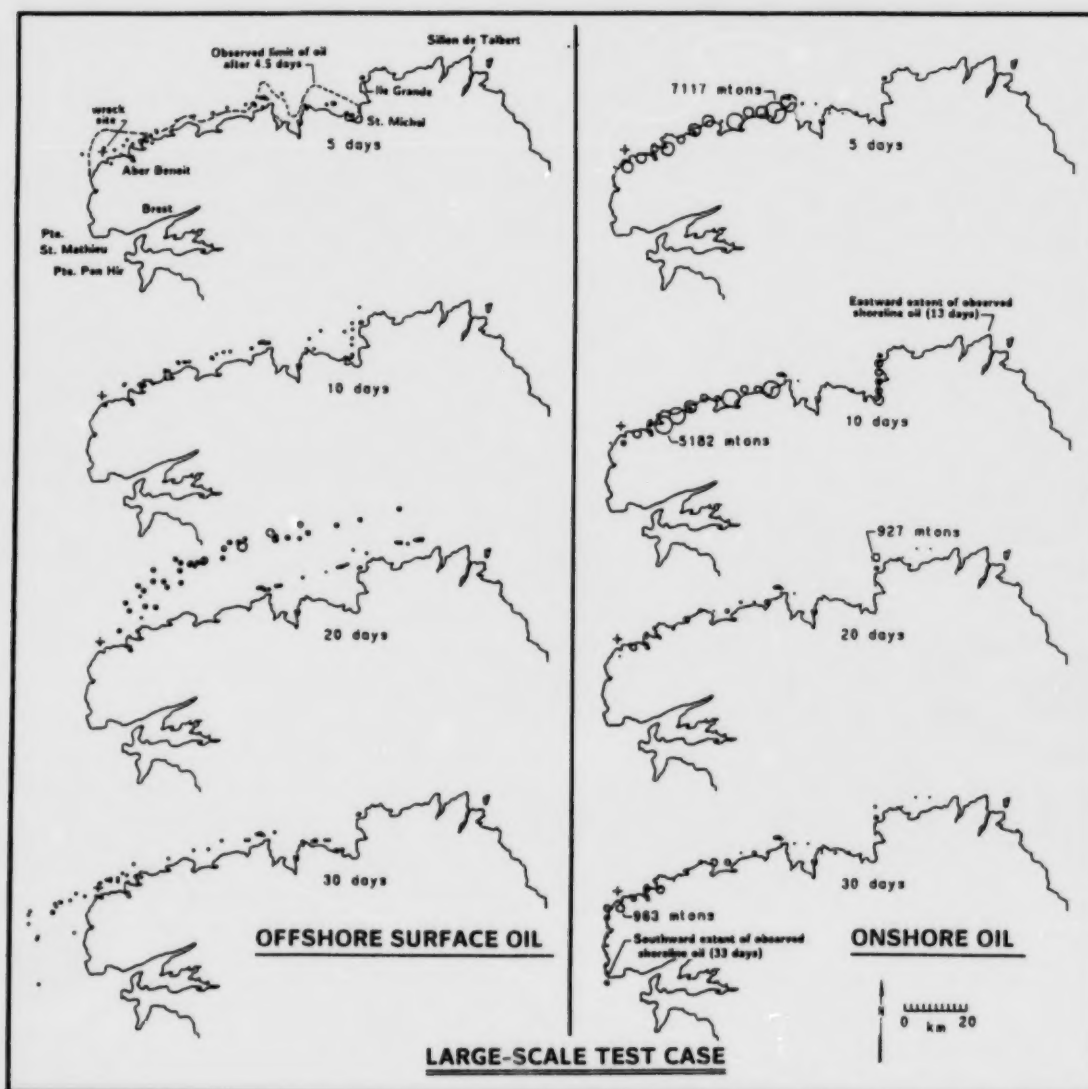


Figure 10. Distribution of offshore surface oil and onshore oil (foreshore surface and backshore) for the large-scale test case. Offshore, circles indicate computed areal coverage of thick oil. Onshore, circles are proportional to the oil mass associated with each grid cell. The maximum value of the circle for each time plot is given.

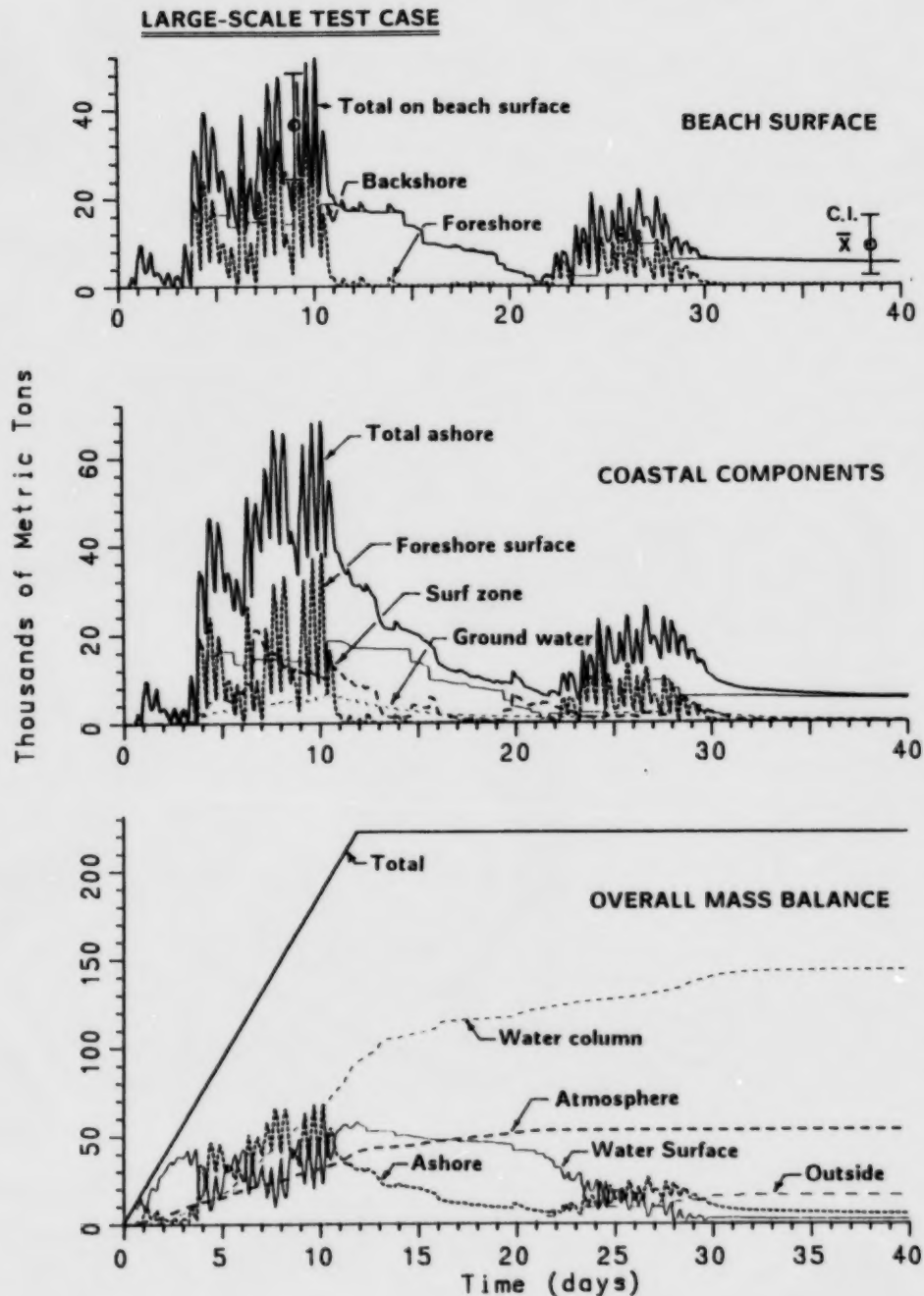


Figure 11. Dynamic mass balances (overall, coastal components, and beach surface) for oil associated with the large-scale test case. A second heavy oiling of the shoreline, reflected in the observations but not in the small-scale test results, is visible between days 23 and 28. Observed values of oil quantity on the shoreline and 95% confidence intervals are indicated in the top diagram.

CONCLUSIONS

Two tests cases of the COZOIL model against the Amoco Cadiz data set have been performed. In general, the model effectively reproduced the offshore and onshore distribution of the Amoco Cadiz oilspill. Mass balance distributions were also simulated realistically, considered from a variety of viewpoints. The lifting of oil off the intertidal beach surface and its redeposition on a falling tide under appropriate wind conditions show clearly in the mass balance time series plots.

The small-scale test case, with relatively detailed resolution of the coastline adjacent to the site appropriately reproduced onshore and offshore surface oil distributions, but generally placed too much oil onshore, perhaps due to a too slow removal rate and the lack of correct hydrodynamics (i.e. including storm surge). The limited boundaries also inhibited the model from effectively reproducing the subsequent redeposition of oil after being transported offshore by winds. On a very fine scale of 0.5 km, the model reproduced the general variance noted in the Amoco Cadiz spill incident, and came close to observed values at three particular stations. Variations in oil quantities onshore within specific grid cells can be lessened by grouping together oil within the grid cells composing the same shoreline reach.

The large-scale test case, using only 11 shoreline segments over the entire area, portrayed the overall distribution of offshore and onshore oil quite well, but fell about 30 km short in the eastern migration of the oil, perhaps due again to inaccurate hydrodynamics. The mass balance of onshore oil quite realistically depicts the actual spill case and compares well with observations.

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MODELLING THE FATE OF HYDROCARBONS IN OIL SPILLS AND WATER

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ABSTRACT

A model of hydrocarbon fate in oil spills and water based on the concept of fugacity, QWAFI, is applied to results of a simulated oil spill using LOTUS 1-2-3 on a microcomputer. QWAFI is a modification of the QWASI model in which the sediment compartment has been replaced by an oil compartment. The QWAFI approach is believed to be capable of correlating and predicting concentrations of specific hydrocarbons in the oil slick and in the water column as a function of time. The results are sufficiently accurate for environmental purposes, e.g. for toxicity assessment. The model is readily applicable to any number of hydrocarbons for which initial oil concentrations and physical-chemical data are available.

INTRODUCTION

When oil is spilled on the sea surface, it is subject to a number of weathering processes including evaporation, dissolution, photolysis and the formation of oil-in-water and water-in-oil emulsions (National Academy of Sciences, 1985). Various models have been proposed to describe these processes and thus provide information on the extent to which marine organisms are exposed to whole oil and to specific hydrocarbons. Of particular interest is the dissolution process by which certain hydrocarbons, notably the low molecular weight aromatics achieve concentrations in the water column which are potentially toxic or bioaccumulative. Estimating concentrations in water is difficult because these hydrocarbons are subject to competitive evaporation and dissolution and because the relative rates of these processes are not always known.

Guidance can be obtained from experiments in which oil is spilled on water under controlled and closely monitored conditions. Examples are the studies of Smith and McIntyre (1971), Harrison et al. (1975), and McAuliffe (1977) which examined the relative importance of evaporation versus dissolution for various compounds.

However, until the experiments of Payne et al. (1981), a comprehensive set of data on the simultaneous effects of

evaporation and dissolution on oil weathering and on specific hydrocarbons was not available. Payne et al. investigated compound-specific evaporation and dissolution in laboratory and field experiments to yield a data set that is critical not only for input to oil-weathering computer models but also for verification of predicted output.

Our group has been working for some years on developing a set of models describing the fate of chemicals in the aquatic environment. A mathematical model, based on the fugacity concept, which quantifies diverse environmental processes has been devised and tested. This model is termed the Quantitative Water, Air, Sediment Interaction or QWASI model (Mackay et al., 1983). QWASI has been especially useful for describing the fate of chemicals such as pesticides in ponds and lakes.

Recently, we endeavoured to apply the QWASI model to pyrethroid chemicals which are applied as emulsions to the water surface, in effect forming a "slick" or "film". The extent to which fish and other aquatic organisms are exposed to pyrethroid chemicals is thus strongly influenced by the fate of the chemical as it migrates from the surface film. In attempting to model this phenomenon, we have borrowed many ideas and information from oil spill studies. The pyrethroid slick and the oil spill are essentially the same problem with the exception that in the case of oil spills we are treating a mixture of hundreds of chemicals. But with the wide availability of fast personal computers able to do a multitude of calculations in seconds, this is merely a delaying inconvenience and is not really an impediment to understanding.

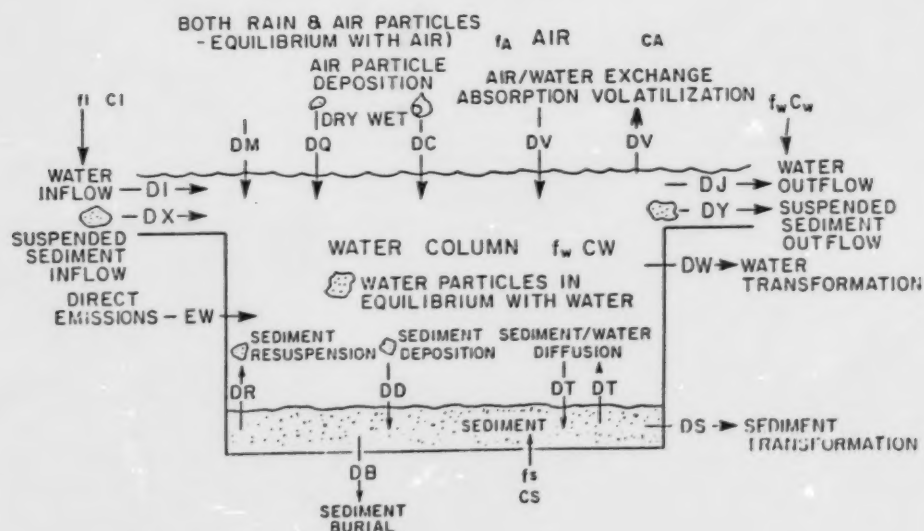


Figure 1. QWASI Fugacity Model Processes

In this paper, we explore how the QWASI model, modified to include consideration of a surface film, can be used to elucidate the fate of specific hydrocarbons in a slick. The air-film-water system is analogous to the air-water-sediment system treated in the QWASI model (Figure 1); that is, it is mathematically similar to the QWASI model. This analog to the QWASI model is termed the QWAFI model (Figure 2).

Presently, we are integrating QWASI and QWAFI into a comprehensive model, termed QWASFI (Figure 3), the Quantitative Water Air Sediment Film Interaction model. QWASFI describes the fate of a chemical in an air-film-water-sediment system.

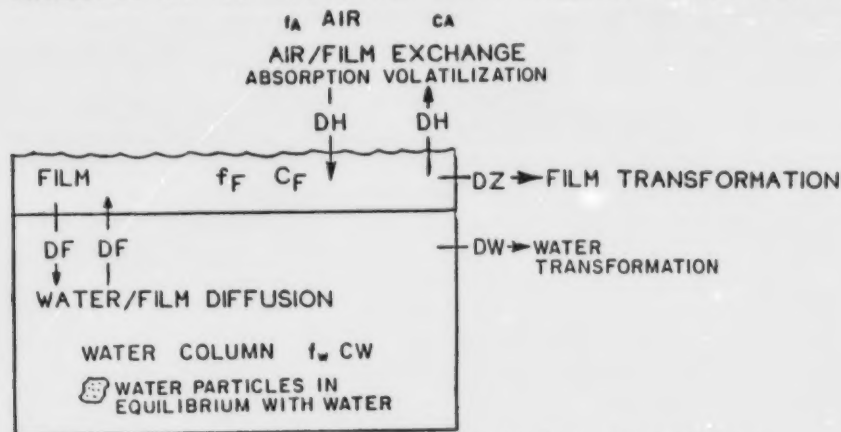


Figure 2. QWAFI Fugacity Model Processes

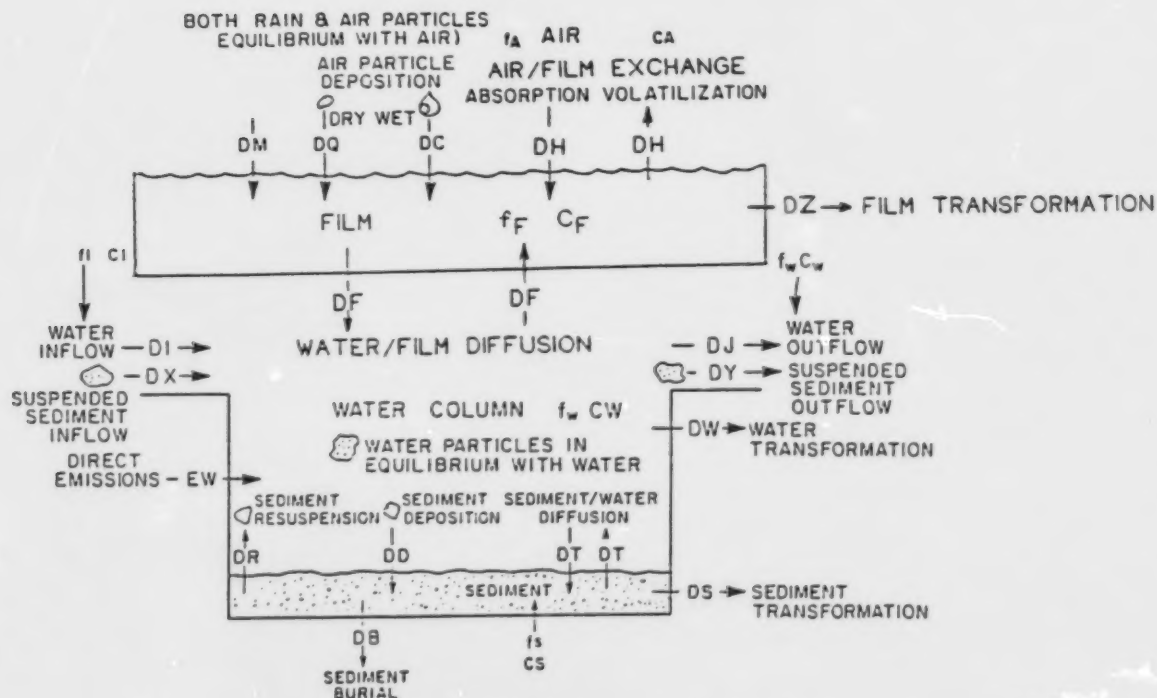


Figure 3. QWASFI Fugacity Model Processes

The approach in this paper is to (i) describe the model briefly in terms of its underlying equations and processes simulated, and (ii) outline its application to simulated oil spill data generated by Payne et al. (1981).

MODEL DEVELOPMENT

Equations

The processes considered in QWAFI are illustrated in Figure 2. To simplify the algebra, fugacity is adopted instead of concentration as the driving force behind the processes (Mackay et al., 1983). The resulting equations can be treated in algebraically identical but more cumbersome concentration terms. Definitions of the symbols used are given in Table 1.

For each medium, the concentration C (mol/m^3) is related to fugacity f (Pa) using a fugacity capacity term Z ($\text{mol}/\text{m}^3 \cdot \text{Pa}$) which is specific to the chemical, the medium and prevailing temperature. The relationship is that C equals Zf .

Table 1
Definition of Symbols

Quantity	
A	area (m^2)
C	concentration (mol/m^3)
D	transport/transformation parameter ($\text{mol}/\text{Pa} \cdot \text{h}$)
f	fugacity (Pa)
G	flow rate (m^3/h)
H	Henry's Law Constant ($\text{Pa} \cdot \text{m}^3/\text{mol}$)
I	group of D variables
J	flowrate per unit area ($\text{m}^3/\text{m}^2 \cdot \text{h}$)
k	rate constant (h^{-1})
K	mass transfer coefficient (m/h)
R	gas constant ($8.314 \text{ Pa} \cdot \text{m}^3/\text{mol} \cdot \text{K}$)
T	temperature (K)
V	volume (m^3)
Z	fugacity capacity ($\text{mol}/\text{m}^3 \cdot \text{Pa}$)
Subscripts	
A	air
E	film in equilibrium with air at air-film surface
F	oil film
G	water in equilibrium with oil film at film surface
H	film-to-air or air-to-film transfer
L	liquid phase
P	suspended sediment particles
T	water-to-film or film-to-water transfer
V	volatilization
W	water
Z	transformation in film

Values for Z are calculated from the partitioning and physical/chemical properties as shown in Table 2. Z for the oil film is calculated assuming that the oil film has the same physical/chemical properties as a film of octanol. Therefore, K_{OW} is equal to Z_F/Z_W and Z_F is equal to $K_{OW}Z_W$.

Table 3 illustrates how process rates can be equivalently expressed as a function of concentrations or fugacity. In the latter case, "D" values are used such that the rate is D_f (mol/h) and D has the units of mol/Pa.h. D values can also be grouped as shown in Table 3 (D_1 through D_5) to represent aggregate rates of chemical transfer into or out of various compartments. An important feature of this is that processes which affect transport and transformation and which vary greatly in nature are expressed in a common system of units (D values) such that rates can be compared directly.

Table 2
Definition of Fugacity Capacities

Compartment	Definition of Z (mol/m ³ .Pa)
Air	$Z_A = 1/RT$ where $R = 8.314 \text{ Pa.m}^3/\text{mol.K}$ $T = \text{temperature (K)}$
Film	$Z_F = K_{OW}Z_W$ where $K_{OW} = \text{octanol-water partition coefficient}$ $Z_W = \text{fugacity capacity for water}$
Water	$Z_W = 1/H \text{ or } C^S/PS$ where $C^S = \text{aqueous solubility (mol/m}^3\text{)}$ $PS = \text{vapour pressure (Pa)}$ $H = \text{Henry's Law constant (Pa.m}^3/\text{mol)}$
Solid Sorbent (sediment, soil, or particles)	$Z_p = K_{SW}PS/H$ where $K_{SW} = \text{partition coefficient (litre/kg)}$ $ps = \text{density (kg/litre)}$

Table 3
QWAFI Model Processes and Rate Expressions

Process	Rates (mol/h)			D and D Group
Water Transformation	$V_W C_W k_W$	$V_W Z_W k_W f_W$	$D_W f_W$	$D_W = V_W Z_W k_W$ D ₁
Water-To-Film Diffusion	$K_T A_W C_W$	$K_T A_W Z_W f_W$	$D_T f_W$	$D_T = K_T A_W Z_W$ D ₂
Film-To-Water Diffusion	$K_T A_W C_F$	$K_T A_W Z_W f_F$	$D_T f_F$	$D_T = K_T A_W Z_W$ D ₃
Film Transformation	$V_F C_F k_F$	$V_F Z_F k_F f_F$	$D_Z f_F$	$D_Z = V_F Z_F k_F$ D ₄
Film-To-Air Volatilization	$K_V A_F C_F$	$K_V A_F Z_F f_F$	$D_H f_F$	
Air-To-Film Absorption	$K_V A_F C_E$	$K_V A_F Z_F f_A$	$D_H f_A$	$D_H = K_V A_F Z_F$ D ₅

Unsteady state mass balance equations can be written as follows in differential form:

$$d(f_F)/dt = [f_W D_2 + f_A D_5 - f_F (D_3 + D_4)] / (V_F Z_F) \quad (1)$$

and

$$d(f_W)/dt = [f_F D_3 - f_W (D_1 + D_2)] / (V_W Z_W + V_P Z_P) \quad (2)$$

This pair of equations can be written more compactly as

$$d(f_F)/dt = I_1 + I_2 f_W - I_3 f_F \quad (3)$$

and

$$d(f_W)/dt = I_4 f_F - I_5 f_W \quad (4)$$

$$\text{where } I_1 = (f_A D_5) / (V_F Z_F) \quad (5)$$

$$I_2 = D_2 / (V_F Z_F) \quad (6)$$

$$I_3 = (D_3 + D_4) / (V_F Z_F) \quad (7)$$

$$I_4 = D_3 / (V_W Z_W + V_P Z_P) \quad (8)$$

$$I_5 = (D_1 + D_2) / (V_W Z_W + V_P Z_P) \quad (9)$$

The solutions to the above equations, with initial conditions f_{W0} and f_{F0} are:

$$f_F = f_{F\infty} + I_8 \exp(-(I_6 - I_7)t) + I_9 \exp(-(I_6 + I_7)t) \quad (10)$$

$$f_W = f_{W\infty} + [(I_3 - I_6 + I_7) I_8 \exp(-(I_6 - I_7)t) + (I_3 - I_6 - I_7) I_9 \exp(-(I_6 + I_7)t)] / I_2 \quad (11)$$

$$\text{where } f_{F\infty} = I_1 I_5 / (I_3 I_5 - I_2 I_4) \quad (12)$$

$$f_{W\infty} = I_1 I_4 / (I_3 I_5 - I_2 I_4) \quad (13)$$

$$I_6 = (I_3 + I_5) / 2 \quad (14)$$

$$I_7 = [((I_3 - I_5)^2 + 4 I_2 I_4)^{0.5}] / 2 \quad (15)$$

$$I_8 = [-I_2 (f_{W\infty} - f_{W0}) + (I_3 - I_6 - I_7) (f_{F\infty} - f_{F0})] / 2 I_7 \quad (16)$$

$$I_9 = [I_2(f_{w\infty} - f_{w0}) - (I_3 - I_6 + I_7)(f_{f\infty} - f_{f0})]/2I_7 \quad (17)$$

These equations thus describe the changing film and water fugacities with time from initial values of f_{f0} and f_{w0} to $f_{f\infty}$ and $f_{w\infty}$ at infinite time.

From these fugacities, the concentrations are calculated as Zf where Z is the appropriate Z value. Concentrations in suspended matter can be deduced as $f_w Z_p$.

In summary, from input data of volumes, Z values, D values and initial concentrations in the oil film and in the water (from which the initial fugacities are calculated), the concentration history in the film and in the water can be deduced. The task is to select the parameters which control the Z and D values to give a satisfactory fit between experiment and model.

Microcomputer Model

QWAFI on LOTUS is an adaptation of QWASI on LOTUS (Southwood et al., 1988), a LOTUS 1-2-3 spreadsheet programmed with the model equations. LOTUS 1-2-3 is well-suited for interactive calibration and testing of models and was selected due to its combination of powerful features such as macro commands, its ease of use, and graphics capabilities.

QWAFI on LOTUS is set up such that the user enters basic physical-chemical data such as molecular weight, octanol-water partition coefficients, and variables related to reaction rates. The program uses these inputs to calculate D values and resulting concentrations in water and sediment are performed. Graphs of observed and simulated concentrations versus time for water and for film are automatically generated using a macro command. These graphs, and the structure of the spreadsheet, allow the modeller to assess rapidly the relative importance of different physical processes, for example reaction or volatilization, and guide the user towards focussing attention on changes to appropriate inputs to improve the "fit" of the simulation. This iterative process requires the modeller to have initial estimates of realistic ranges of values to use for the various inputs. If desired, the user may also complement the visual assessment of the simulation with a numerical approach.

The spreadsheet is set out in two parts. One portion contains the variables, called primary inputs; the other portion contains the formulae and the results. There is space for a maximum of twenty data points each for the film and for the water but this could be expanded if desired. Data for biotic concentrations could also be added.

The general procedure, illustrated in Figure 4, is for the modeller to assemble an initial set of primary estimated (possibly guessed) values of the primary variables such as physical chemical properties, rate constants and flow rates which control the chemical's fate. These are converted into Z values, D values and D value groups, from which the modelled fate is deduced. At each stage of calculation, scaling factors are introduced which the modeller may use to adjust subsequently calculated values. These scaling factors are initially set at 1.0. By redefining a factor as 2.0, the user may test the effect

of doubling, for example, a rate constant, a D value, or a D group.

The modeller compares the computed and experimental concentrations as a function of time and adjusts the scaling factors until a satisfactory fit is obtained. This process may involve exploratory sensitivity analyses and trial and error setting of scaling factors. Adjustment is done first to the D group factors, then to the individual D value factors to account for the required group factor, then to the primary factors. Ultimately a fit is obtained by adjusting only the primary factors. This systematic tiered approach eliminates the problem of attempting to adjust perhaps 20 variables to achieve the desired fit.

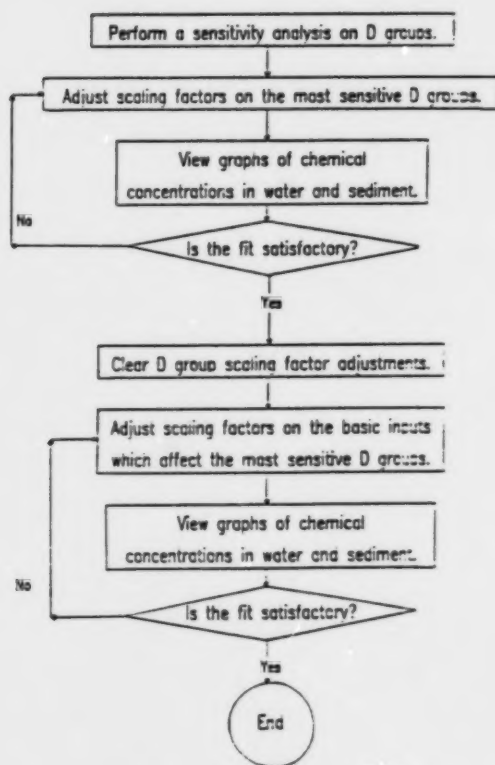


Figure 4. Flowchart of the QWASI on LOTUS Approach

MODEL APPLICATION

The model was applied to data generated by Payne et al. (1981) with the evaporation/dissolution chamber shown in Figure 5. The chamber was constructed to allow simultaneous compound-specific concentration determinations in air, oil and water phases such that evaporative and dissolution process rates could be determined as a function of time (Payne et al., 1981). The three schematic diagrams in Figure 6 show the chamber's component parts and dimensions. The air circulation system allows air to pass over the slick on a one-time basis so that approximately 90% of the air flow is diverted up the exhaust vent. The tank has been fabricated from glass, stainless steel, anodized aluminum and teflon to minimize sample contamination. The circular design was chosen so that oil driven by the air flow would not accumulate at one end of the chamber. To assure homogeneity in the water column, the water is agitated from below by means of a rotating paddle. Data required by the QWAFI spreadsheet regarding the chamber is listed in Table 4.

Oil weathering experiments in the chamber were undertaken with Prudhoe Bay crude oil at ambient temperatures, 19 to 23°C. Samples collected from the oil film and from the water were analyzed to determine concentration changes with time for specific compounds in each phase. Concentration data for five of these compounds were compared with QWAFI predictions.

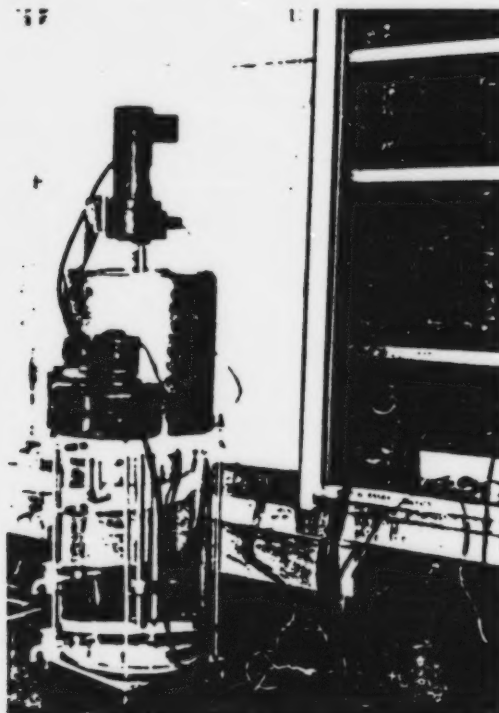


Figure 5. Assembled Evaporation/Dissolution Chamber. Reprinted from Payne et al. (1981).

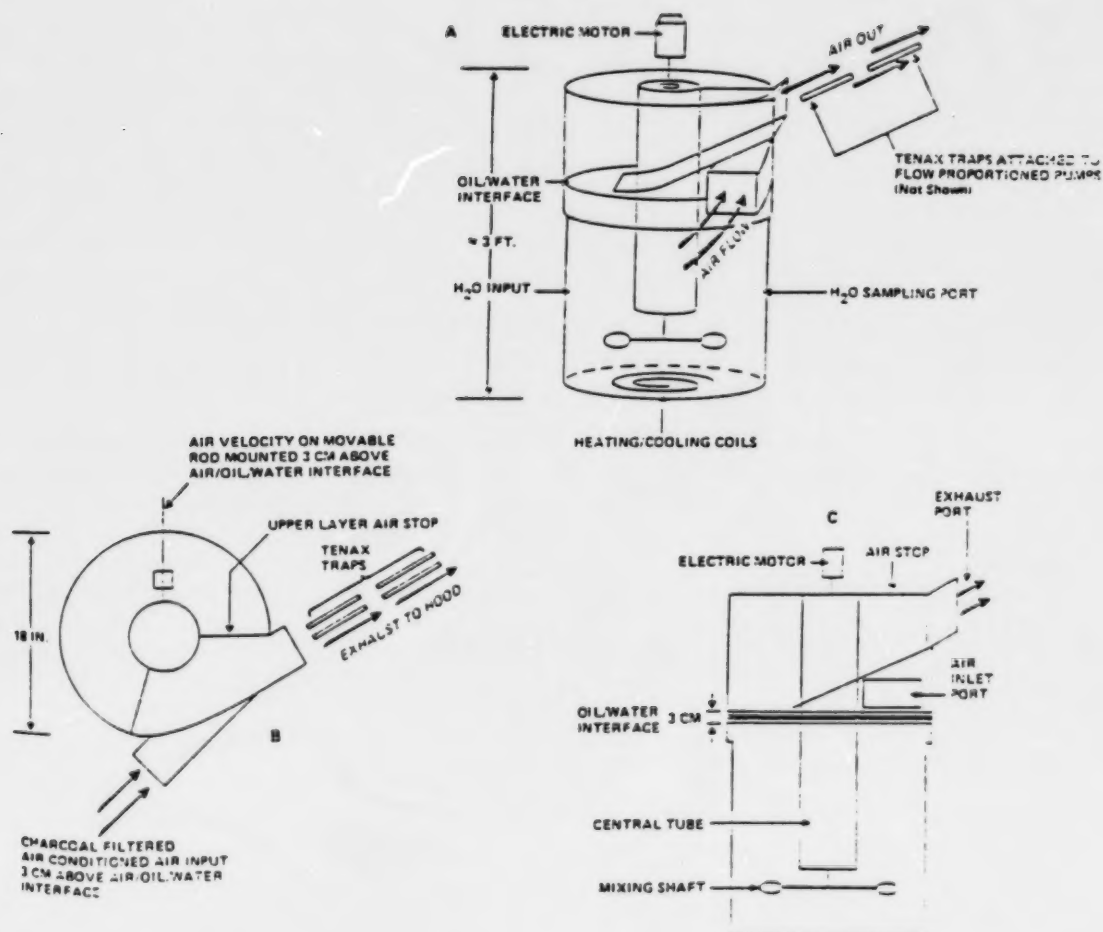


Figure 6. Prototype Tank Design for Evaporation/Dissolution Experiments. Reprinted from Payne et al. (1981).

Table 4
Properties of the Evaporation/Dissolution Chamber

Temperature (K)	292
Volumes (m ³)	
Water	7.51×10^{-2}
Film	4.93×10^{-3}
Suspended sediment	0
Areas (m ²)	
Air-film interface	0.164
Film-water interface	0.164

Table 5
Primary Inputs

	Ethylbenzene	o-Xylene	p-Xylene	Naphthalene	Biphenyl
Molecular mass (g/mol)	106.17	106.17	106.17	128.2	154.21
Vapour Pressure (Pa)	933	667	867	30.7	8
Solubility (mol/m³)	1.05	1.22	1.04	0.156	0.0309
log K_{OW}	3.13	3.13	3.18	3.01	3.70
Mass Transfer Coefficients (MTC) (m/h)					
Air-side	18.7	18.7	18.7	17.7	15.5
Film-side	0.23	0.23	0.23	0.21	0.19
Water-side	0.23	0.23	0.23	0.21	0.19
Rate Constants (h⁻¹)					
Transformation in film	0	0	0	0	0
Transformation in water	0	0	0	0	0
Initial Concentrations					
Air (mol/m ³)	0	0	0	0	0
Film (ng/ml or ug/L)	24210	102600	165600	472500	145800
Water (ng/ml or ug/L)	0	0	0	0	0

Data required by the QWAFI spreadsheet for these compounds are listed in Table 5. Vapour pressures for ethylbenzene, o-xylene and p-xylene are from Verscheuren (1983); vapour pressures for naphthalene and biphenyl are from Lyman (1982). Solubilities in seawater for ethylbenzene, o-xylene and p-xylene are from Sutton and Calder (1975); the solubility of naphthalene in seawater is from Verschueren; the solubility of biphenyl in seawater is from Clark and MacLeod (1977). Miller (1985) gives the log K_{OW} 's for ethylbenzene, o-xylene and p-xylene; Verscheuren gives the log K_{OW} for naphthalene and gives a range of log K_{OW} 's between 3.16 and 4.09 for biphenyl.

Secondary values calculated by QWAFI on LOTUS are listed in Table 6.

Plots of Payne et al.'s observed results and QWAFI predictions are shown in Figures 7 to 16.

Table 6
Secondary Values Calculated in QWAFI on LOTUS

Physical Properties
H ($\text{Pa} \cdot \text{m}^3/\text{mol}$)

Inputs for Calculation of Z
K_p for sediment (L/kg)
K_p for air particles

Z Values ($\text{mol}/\text{m}^3 \cdot \text{Pa}$)
Z for air
Z for water
Z for suspended sediment

Fugacity (Pa)
Air fugacity
Initial film fugacity
Initial water fugacity

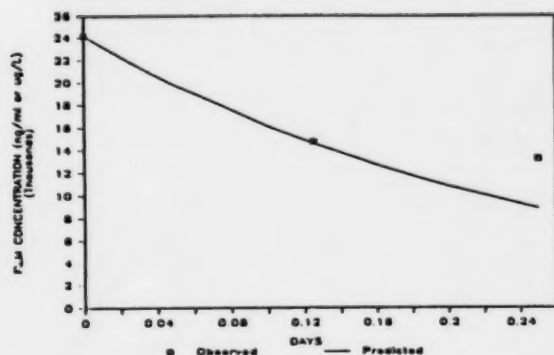


Figure 7. Concentration of Ethylbenzene in the Oil Film versus Time

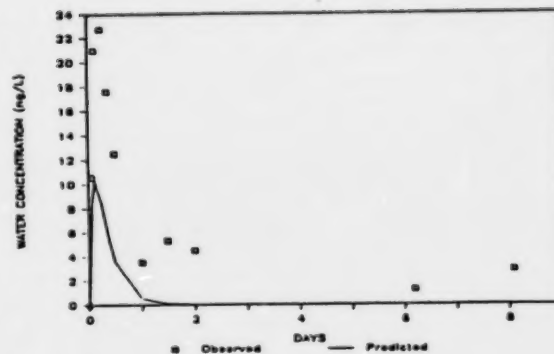


Figure 8. Concentration of Ethylbenzene in the Water Column versus Time

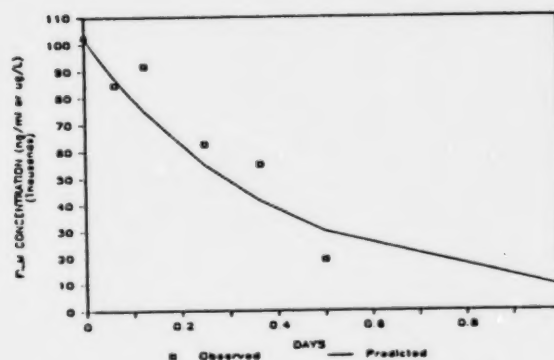


Figure 9. Concentration of o-Xylene in the Oil Film versus Time

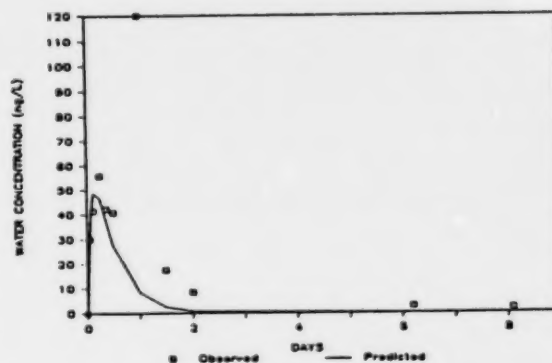


Figure 10. Concentration of o-Xylene in the Water Column versus Time

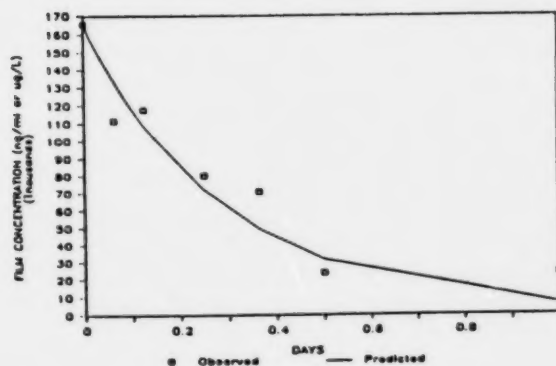


Figure 11. Concentration of p-Xylene in the Oil Film versus Time

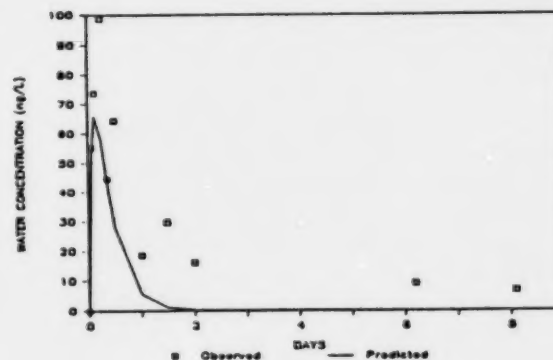


Figure 12. Concentration of p-Xylene in the Water Column versus Time

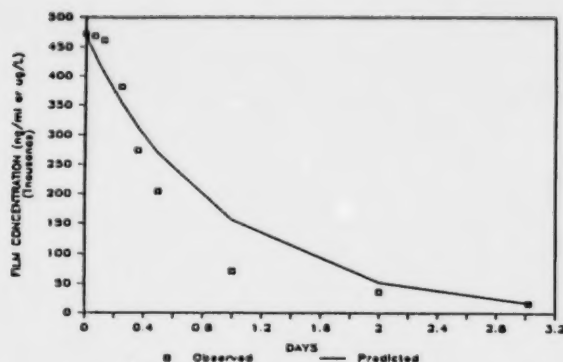


Figure 13. Concentration of Naphthalene in the Oil Film versus Time

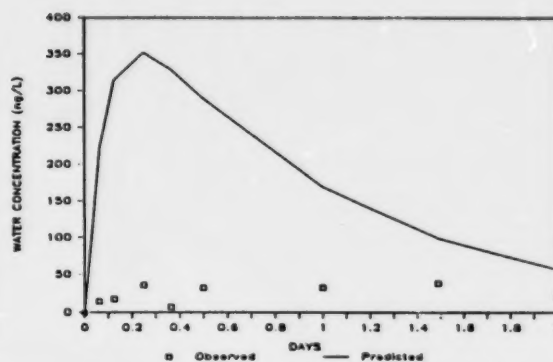


Figure 14. Concentration of Naphthalene in the Water Column versus Time

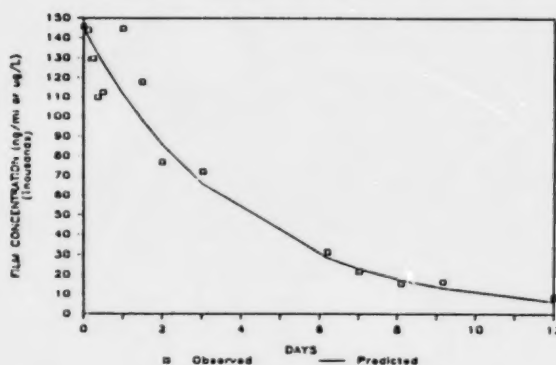


Figure 15. Concentration of Biphenyl in the Oil Film versus Time

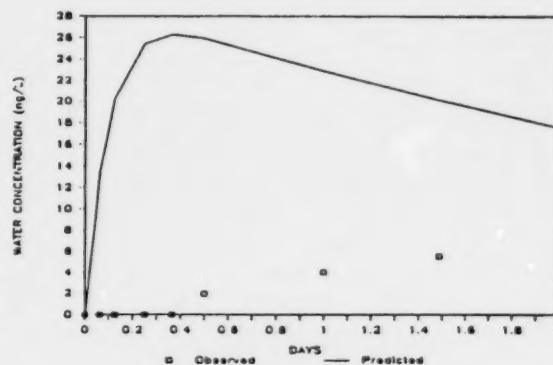


Figure 16. Concentration of Biphenyl in the Water Column versus Time

DISCUSSION AND CONCLUSIONS

The application of the QWAFI model to Payne et al.'s data for ethylbenzene, o-xylene, p-xylene, naphthalene and biphenyl demonstrates that the model is able to provide order of magnitude estimates of concentrations of chemicals resulting in water after an oil spill. Although QWAFI consistently underpredicts water concentrations for the low molecular weight aromatics and overpredicts water concentrations for aromatics of higher molecular weight, the approach seems to be capable of yielding results which are sufficiently accurate for most environmental purposes. Some of the deviation in the case of the higher molecular weight hydrocarbons is likely attributable to error in

the oil-water partition coefficient. The use of the octanol-water partition coefficient appears to be a reasonable first approximation but more accurate oil-water partition coefficients are obviously preferable.

The principle conclusion is that this methodology has the potential to describe the fate of hydrocarbons in slicks and water. Some points are worthy of note:

(1) A high level of accuracy is not needed in these simulations because environmental conditions always contain a large degree of uncertainty. Even an approximate quantification of this type:

"50 to 70% of hydrocarbon X will evaporate in 24 hours
and 5 to 8% will dissolve leaving 22 to 45% in the
slick and yielding water concentrations in the range
0.03 to 0.10 mg/L"

is a considerable advance in current capabilities of quantifying hydrocarbon fate. Further, it is sufficiently accurate for most assessment purposes.

(2) Having been established, the model can be easily applied to any number of hydrocarbons. The only hydrocarbon-specific information needed is the initial concentrations and its physical-chemical properties.

(3) An attractive option is to calibrate the model with selected "benchmark" chemicals. This is essentially the approach used by Harrison et al. (1975).

(4) The model includes the potential to express rates of hydrocarbon transformation by photolysis, biodegradation etc. These processes are more important in the long term, thus it may be desirable to run the model in different time "phases", i.e. short term and long term versions.

(5) We believe that the model could be applied to other laboratory tests, tank tests, pond tests, ocean enclosures such as CEPEX systems, and to open ocean spills. Often such experiments generate a great deal of data which is under-interpreted and under-utilized.

(6) Finally, the model provides a method of characterizing and correlating data on concentrations and times and expressing them as exposures. An interesting option is to develop equations for organism response (e.g. toxicity) as a function of exposure, then test how the estimated exposures will result in toxic responses. Obviously it will be necessary to treat the additive effects of the many hydrocarbons which are present in water which has contacted the slick.

In general, we believe that novel models such as this have the capability of providing a better quantification and a better understanding of the fate and effects of specific hydrocarbons in the vicinity of slicks and thus provide a more accurate

assessment of their potential to cause environmental or ecological damage.

A copy of the program which can be run in conjunction with LOTUS 1-2-3 on any IBM PC or IBM compatible is available from Dr. Mackay.

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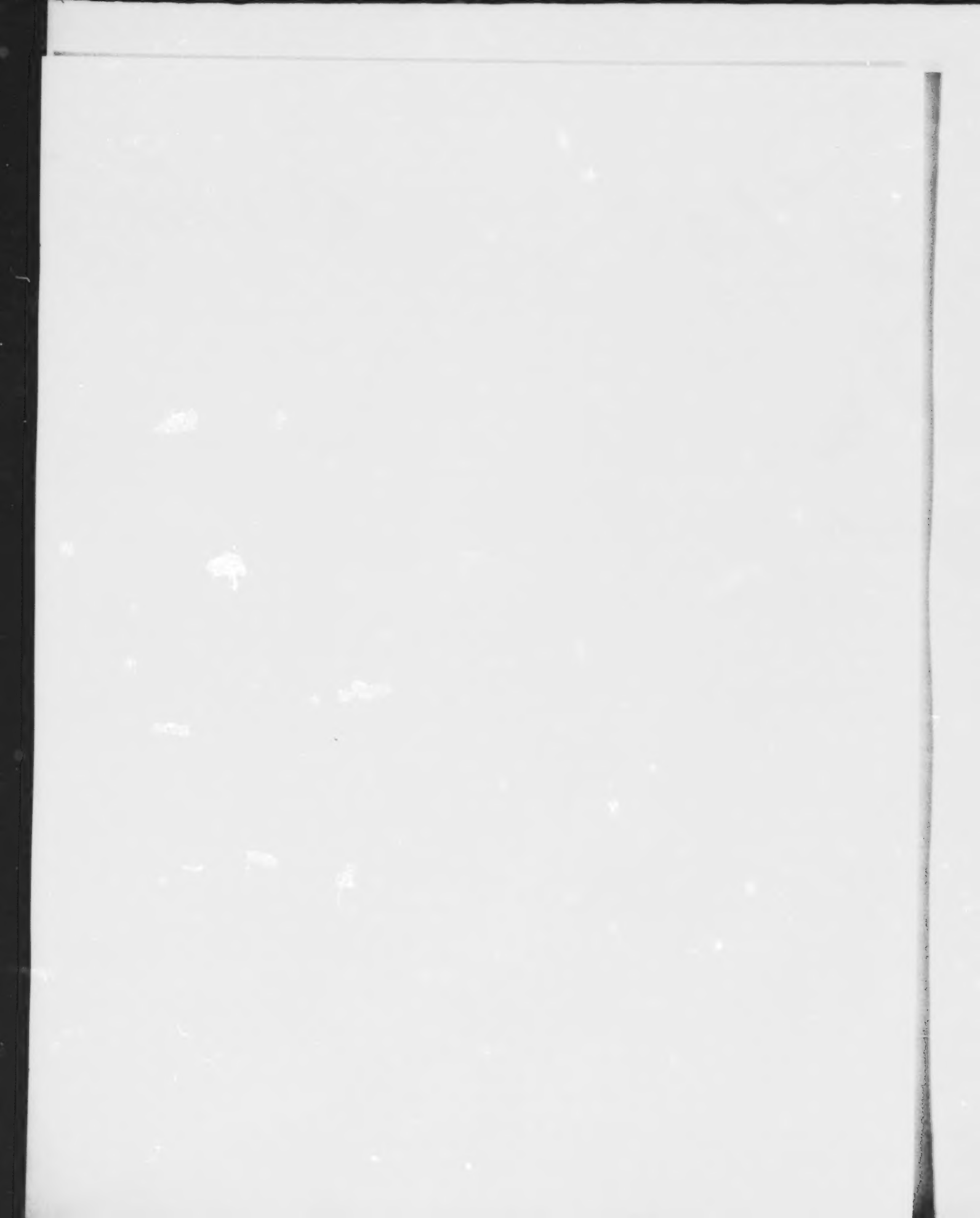
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POLAR LOWS IN THE BEAUFORT SEA

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INTRODUCTION

Forecasters in Scandinavia and Britain have long been aware that small scale vortices frequently develop deep within cold air masses streaming over warm water surfaces. Because these weather systems, known as polar lows, most frequently occur over data sparse ocean areas, are small scale features, develop rapidly, frequently produce gale or near gale force winds and are not adequately handled by the numerical models, they present a major challenge to the operational forecaster. The increase in oil exploration and production off Norway resulted in a demand for improved offshore forecasts which in turn spawned a heightened interest in polar lows. In 1983 the Norwegian Polar Low Project was initiated to advance the knowledge of these enigmas. The three-year project culminated in an International Conference on Polar Lows held from May 20 to 23, 1986 at the Norwegian Meteorological Institute, Oslo.

Synoptic conditions similar to those of the Norwegian Sea exist over the Bering Sea and Gulf of Alaska during the winter months. However, it was not until Businger (1987) that a detailed investigation of the occurrence of polar lows in this area appeared in the literature.

Offshore exploration has been active in the Beaufort Sea since the mid seventies. Although the exploration area is ice bound for much of the year, there is a period during the late summer and fall months when cold arctic air can stream across the warmer water surfaces of the southern Beaufort Sea. It is only natural then that the question of the occurrence of polar lows in the Beaufort Sea should arise. This paper addresses that question.

BACKGROUND THEORY

Despite the ability to observe these systems, primarily through the use of satellite imagery, a theory to fully explain the development of polar lows has yet to emerge.

However, two main classes of vorticies, developing in arctic air masses flowing over warmer water surfaces, have been identified. The first class range in size from the mesoscale to small synoptic scale and form on the cold side but near the polar front. These are essentially a baroclinic phenomena (Reed, 1979). The second class develops well into the arctic air and away from areas of deep baroclinicity and although baroclinic instability may at times play a role, the main driving force is convection. (Rasmussen, 1986).

This requires a conditionally unstable air mass with a significant air/sea temperature difference.

Wilhelmsen (1986) found that air temperatures near the starting position of the 33 cases studied were near -20°C over ice and up to 0°C over water. He also found that rapid pressure rises were common behind the lows with rapid falls in advance of the systems less common. Despite the existence of nearly barotropic conditions at mid and high levels, a strong thermal gradient normally exists in the lower levels due to modification of the cold air mass. (It is this thermal gradient that often results in the inexperienced forecaster introducing a front in a polar low.)

In his paper "The Synoptic Climatology of Polar Low Outbreaks", Businger (1985) presents ten characteristics of polar lows. They are listed below along with an eleventh that is identified later in the same work.

These state that polar lows

- (a) are tight spiral cloud patterns generally asymmetrical, indicative of rotational motion superimposed on slow translational motion.
- (b) are generally limited to the winter half of the year.
- (c) are 200-500 km in diameter.
- (d) form in an air mass that is conditionally unstable through a substantial depth, with below average temperatures at the 50 kilopascal (kPa) level.
- (e) form beneath regions of low geopotential heights, poleward of strong middle and upper tropospheric jet streams.
- (f) form over open water, where strong surface heat and moisture fluxes result in rapid destabilization of the boundary layer.
- (g) tend to fill as they move over land.
- (h) are typically accompanied by convective showers or thunderstorms.
- (i) have the strongest cyclonic circulation near the surface which weakens upward. (This is consistent with the hypothesis that polar lows have a warm core at lower levels. Satellite photographs reveals a clear eye in some cases. [Rasmussen, 1983]).
- (j) form in regions where a secondary, low level baroclinic zone exists.
- (k) have the presence of a weak surface trough as a common feature during the early stages of development.

EXAMPLE OF POLAR DEVELOPMENT

Figure 1 depicts a polar low event in January 1987. A well developed polar low can be seen over the Gulf of Alaska with cold air streaming over the warmer Gulf waters clearly visible. The main frontal zone extends south-southwestward from British Columbia while another major system is evident between the true polar low and the main baroclinic zone. The history of this system was not determined.

Figures 2 and 3 present the surface and 50 kPa charts at 1200 UTC on January 11, 1987 which is nearly the same time as the satellite imagery in Figure 1. Upper air soundings taken at 0000 UTC, January 11, 1987 are presented in Figure 4. The dashed line indicates the result of continued modification from an over water trajectory and may be representative of conditions near the low centre.

The main items to note are

- (a) the system developed well north of the main frontal zone;
- (b) the area of development was in an area where very cold arctic air was flowing over a warmer water surface (water temperatures were near

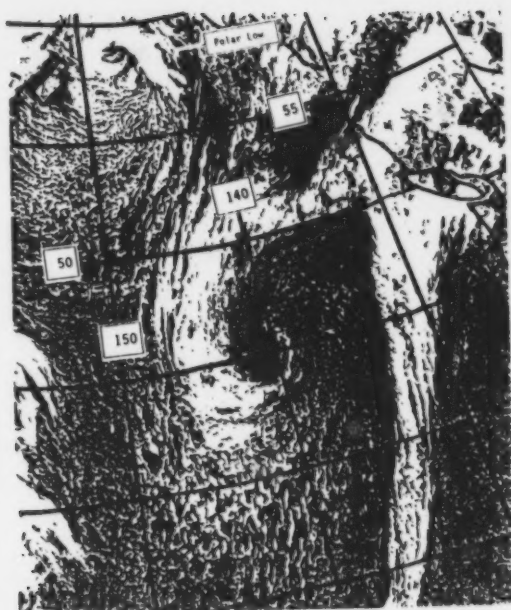


Figure 1. Infra red satellite imagery of Gulf of Alaska. 1243 UTC, January 11, 1987.

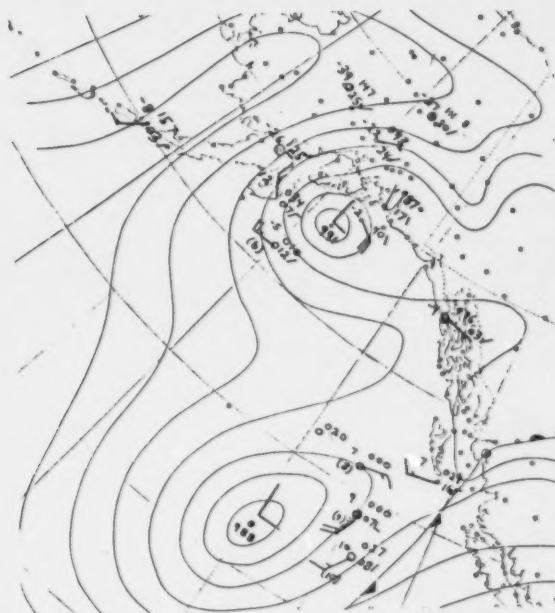


Figure 2. Surface analysis. 1200 UTC, January 11, 1987.

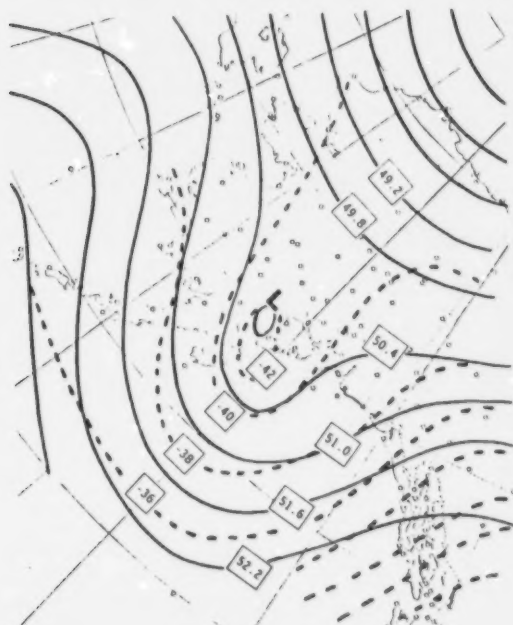


Figure 3. 50 kPa analysis. 1200 UTC, January 11, 1987.

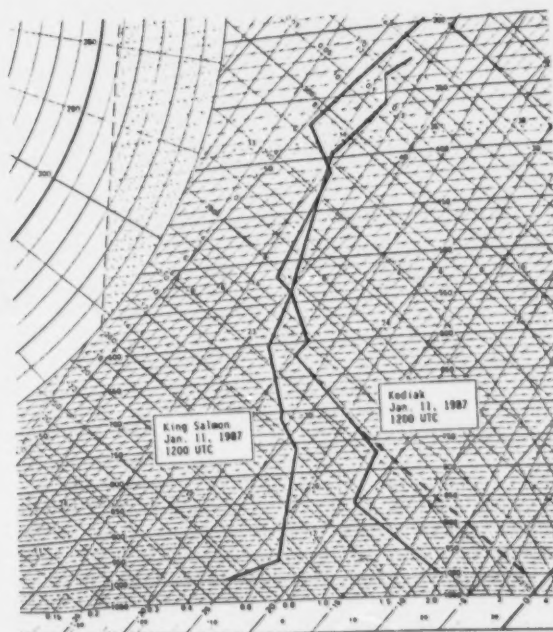


Figure 4. Tephigrams for King Salmon and Kodiak, Alaska. 0000 UTC, January 11, 1987.

- 6°C over the northern Gulf of Alaska and air temperatures over Alaska were below -20°C);
- (c) the surface system developed as an upper cold vortex moved over the area;
 - (d) the air mass at the time of development was conditionally unstable throughout the lower and mid levels of the atmosphere;
 - (e) original satellite pictures showed an area of heavy convective cloud during the time of development; and,
 - (f) the low was preceded by rapid surface pressure falls (maximum of .54 kPa per 3 hrs reported). No rapid rises were evident behind the low although data was sparse. The falls are still within the range of those observed by Wilhelmsen (1986).

EXAMINATION OF BEAUFORT SEA DATA

Methodology

A geographical reference map and map of the study area are presented in Figure 5. Surface analyses produced by the Atmospheric Environment Service forecasters at the Beaufort Weather Office located in Tuktoyaktuk, NWT are available for the period 1976 to 1985. For these years, maps for September, October and November were examined for indications of polar lows. It will



Figure 5. Geographical reference map and study area.

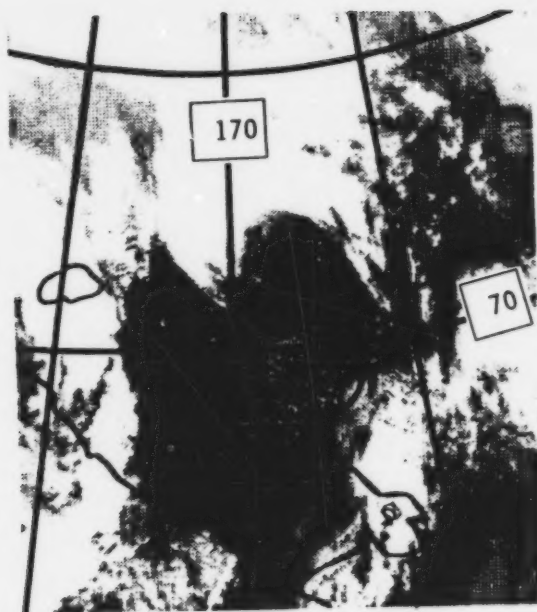


Figure 6. Infra red satellite imagery of Chukchi Sea. 1339 UTC, October 12, 1985.

be noted that a considerable amount of data were available from offshore drill vessels working the southern Beaufort Sea during the period of open water. Sea level pressures transmitted by buoys on the arctic pack ice aided the analysis over the northern areas. NOAA satellite imagery was also examined with particular attention paid to those periods when the surface charts indicated cold air passing across open water in the southern Beaufort Sea.

Results

During the period examined, no instances of polar lows developing over the southern Beaufort Sea were found. One case of a polar low developing over the Chukchi Sea was detected. This system formed in October 1985 and subsequently moved across northwestern Alaska to the study area. Being a particularly intense system and the only example found it will be examined in more detail.

On October 10, 1985 a 98.7-kPa surface low was situated over Novosibirskiye Ostrova. This low and associated upper centre proceeded to move southeast, then eastward, passing between the Russian mainland and Ostrov Vrangelya on October 13, 1987. While a vigorous 50-kPa centre persisted, the surface low weakened to the point where it could no longer be easily analyzed on surface charts. Concurrent satellite imagery indicated a cyclonic circulation east northeast of Ostrov Vrangelya on October 13 with considerable cold air streaming southeastward over the still open water of the Chukchi Sea (Figure 6).

At 0000 UTC, October 14, 1985 a 99.1 kPa surface low was located approximately 175 km west of Barrow with a trough extending southeast then southward across Alaska (Figure 8b). This system developed in response to a 50 kPa short wave trough rotating around the main 50 kPa centre which at that time was located over the western sections of the Chukchi Sea (Figure 8a). This initial low moved across northwest Alaska and into the Beaufort Sea at approximately 75 km/h. Pressures continued to rise west of this system. However, satellite imagery at 2323 UTC on October 13 (Figure 7) indicated a significant change in the nature of the convection occurring over the Chukchi Sea. The area of maximum activity was located southwest of the low visible on October 12. Heavy convection was clearly evident around a centre of rotation near 69.8N and 171.2W. This corresponds to the position of the 50 kPa centre which continued drifting eastward from northeastern Siberia (Figure 8a).

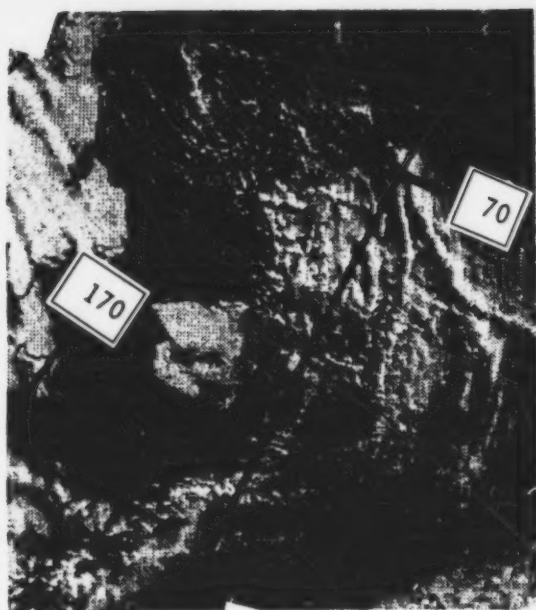


Figure 7. Infra red satellite imagery of Chukchi Sea. 2323 UTC, October 13, 1985.

Figure 9 presents the radiosonde sounding from Barrow at 1200 UTC on October 14, just as the polar low was passing south of the station. The amount of cooling that occurred during the preceding 12 hours is evident by the significant shift to the left of the environmental curve. Upper air data from Ostrov Vrangelya indicated 50 and 70 kPa temperatures of -50°C and -30°C with the upper centre. After adjusting the 1200 UTC ascent from Barrow to allow for low level modification over the Chukchi Sea and for the colder 50 kPa temperatures with the upper center, the potential for deep convection is readily apparent (dashed line on Figure 9). The actual wind profile for Barrow at 1200 UTC (Figure 10) indicated weak cold air advection still occurring below 2.7 km (9 thousand feet) with weak warm advection above 6.1 km (20 thousand feet). Some of the low level cold advection can be explained by the fact that the

trajectory was from land. Weak warm advection was also indicated between 2.7 km and 3.4 km (11 thousand feet), even though the low was still southwest of the station. This, plus the fact that winds in the lower levels decreased with height, may be indicative of a warm core developing in the lower levels of the low.

Surface pressure falls preceded the low by about 225 km with a maximum fall of .36 kPa per three hours reported at Barrow. Barrow also recorded a pressure rise of .52 kPa per 3 hours west of the low. The isallobaric wind resulting from such rises would have contributed to the strong surface winds observed behind the system. These pressure tendencies are also within the range reported by Wilhelmson (1986).

After making landfall the system passed approximately 90 km south of Barrow then moved back over open water passing approximately 110 km north of Prudhoe Bay before moving over the ice pack and weakening (Figures 9c and 9d). Table 1 presents surface winds reported at stations near the path of the low.

Discussion of Results

During the period 1976 to 1985 only one case of a polar low affecting the study area could be identified. No cases of polar lows forming over the open waters of the southeastern Beaufort Sea could be determined. It is postulated that the main reason for this observation is the lack of a sufficient area of open water, especially during the latter portion of the

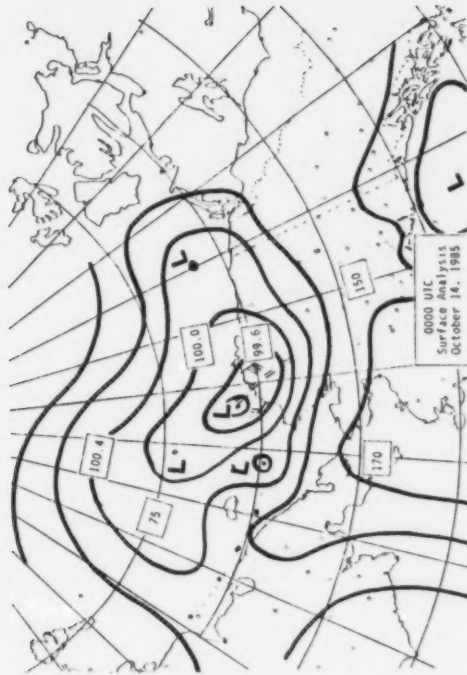


Figure 8(b)

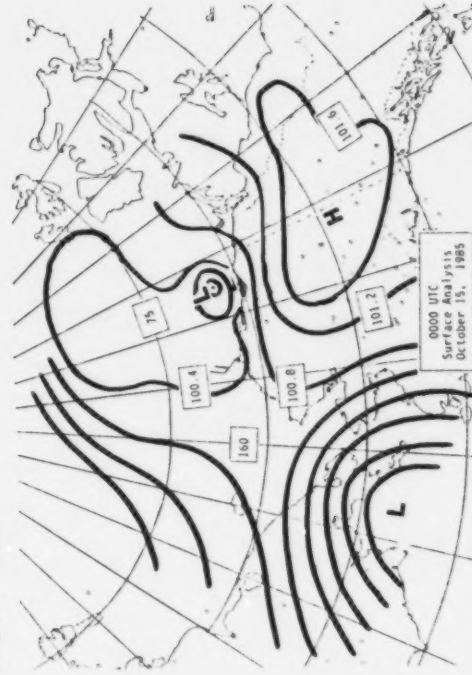


Figure 8(d)

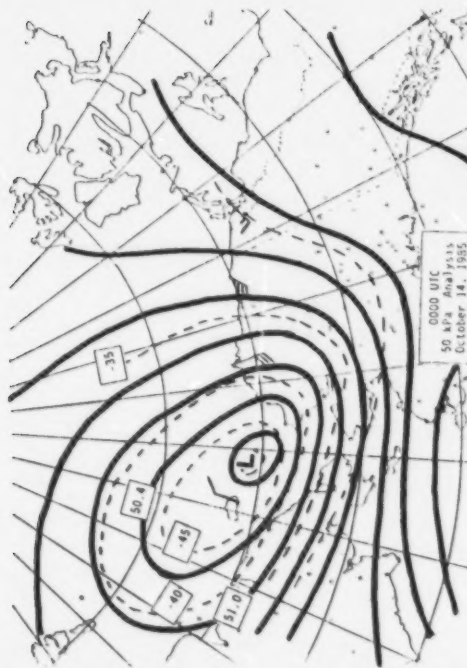


Figure 8(a)

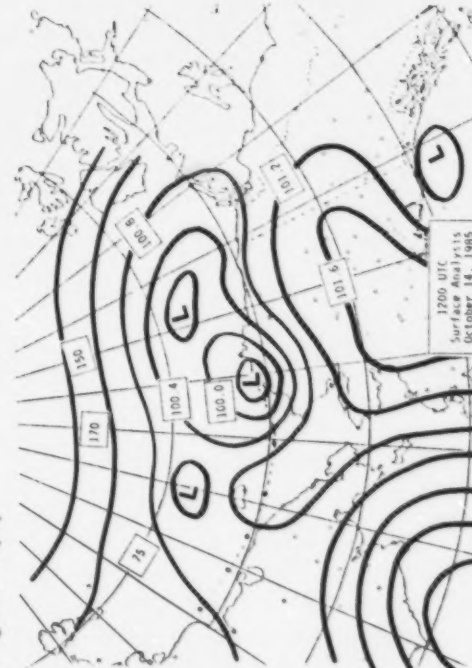


Figure 8(c)

Figure 8. 50 kPa and surface charts for the period October 14-15, 1985.

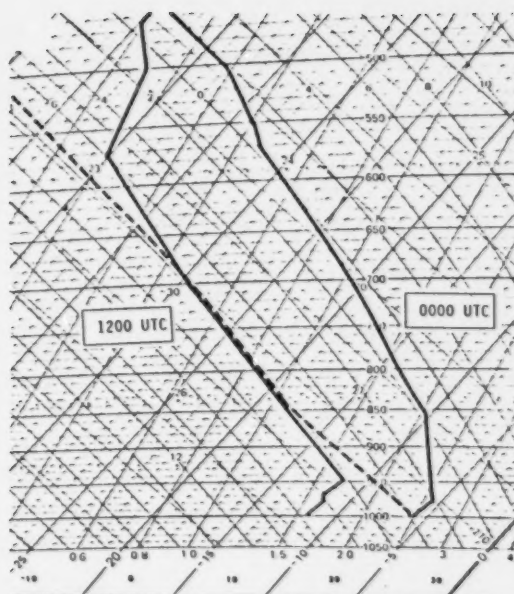


Figure 9. Tephigram soundings for Barrow, Alaska, October 14, 1985.

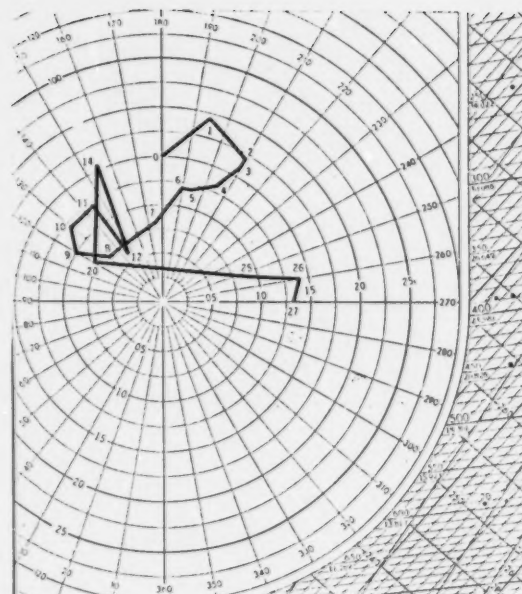


Figure 10. Upper wind profile for Barrow, Alaska, 1200 UTC, October 14, 1985. Units are thousands of feet and knots.

TABLE 1. SURFACE WINDS (KM/H) REPORTED DURING THE OCTOBER 1985 POLAR LOW EVENT.

Date/time	Barrow	Deadhorse	Prudhoe Bay	Explorer 2	Barter Island
14/12	1524	2333		2670	2948G57
13	1326G35	2230G41		2656	2943
14	1028	2333G46	2333G46		2926
15	0428G39	2130	2133		2933
16	0312	2035	2028		2419
17	3437G50	1941	1956		2737
18	3230	2037G44	2128G39		2622
19	3028	1956G76			2219
20	2724	1982G100	2061G96		2519
21	2432	2583G104	2574G100		1939
22	2641G57	2682G100			2561G69
23	2748G67	2765G87	2767G82		2565G76
15/00	3233	2750G65	2750G61		2676G96
01	3028G43	2539G56	2539G56	2793G107	2682G107
02	2539G52	2539G52	2537G48	2774G83	2778G95
03	2920	2343G56	2437G48	2774	2765G80
04	2719	2539G52		2644	2856
05	1722	2443G56		2670	2843
06	2915	2441G56		2674G83	2850G65
07	2513	2437		2674	2952G65
08	3117	2328		2674	2950
09	2915	2324		2674	2943
10	2819	2422		2656	3033
11				2437	3022

Maximum wind gust of 139 km/h reported at Prudhoe Bay. 2035 UTC, October 14, 1985.

year when the supply of cold arctic air increases. Figure 11 indicates the median area of 6/10 or less of ice cover on September 17 and October 15. This amounts to a median northern fetch during mid-September of about 185-275 km with a substantially larger east-west fetch. The northern fetch is then about the same scale as the expected feature, leaving little area for development of low level conditional instability over the water surface. Since development is likely to occur during times of moderate flow, it is reasonable to assume that if a polar low

did begin to form the upper support would move over land or the polar pack before maximum surface development was attained.

An equally important consideration is the lack of conditionally unstable arctic air masses over the Beaufort Sea during the time of minimum ice cover. During September only 0.9% of the upper air assents from Inuvik show an 85 kPa temperature equal to or less than -15°C , a value that would eventually result in conditionally unstable air over the open water of the Beaufort Sea. This only increases to 2.5% at Sachs Harbour. By October the frequency of arctic outbreaks begins to increase and these figures increase to 19.4% at Inuvik and to 29.5% at Sachs Harbour. These figures neither account for account for direction of flow nor do they include any

information about the presence of a 50 kPa trough. The event of October 1985 demonstrates that vigorous polar lows can affect the southwestern Beaufort Sea and that they can strike with little warning. With different synoptic and ice conditions such a low could affect the exploration area of the Canadian Beaufort. During such a scenario it should be possible to provide some advance warning due to distances involved from the development area.

CONCLUSIONS

This study concludes that occurrences of true polar lows in the Canadian Beaufort Sea are rare events. However, this conclusion is based on the examination of only tens years of data and use of a larger data set could alter the results.

Additionally, because of the limited data base over the Chukchi Sea it is possible that other polar lows may have developed but were not detected.

It has been postulated that the main reason for the lack of polar low activity over the southeastern Beaufort Sea is the limited area of open water. A catch 22 being that as the supply of cold arctic air increases during the fall months the area of open water diminishes. Despite this one

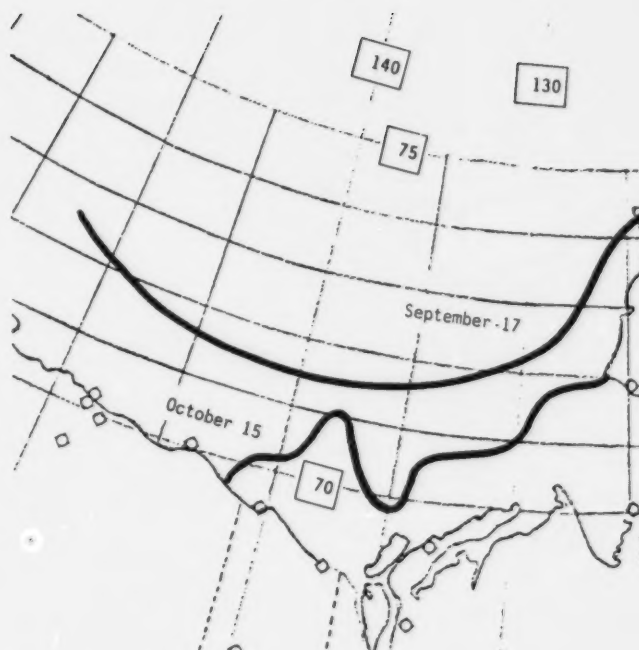


Figure 11. Median position of 6/10 or less of all ice on September 17 and October 15 during the years 1953 - 1978. (after Markham, 1981).

cannot rule out the unusual or rare event. Given optimum synoptic conditions during a year when ice cover is at a minimum it should be possible for a polar low to develop over the southeastern Beaufort Sea. For this reason forecasters must be aware of the factors that contribute to the development of these disturbances otherwise early detection and advanced warning is unlikely. By the same token an understanding of polar lows will assist the forecaster in identifying and correctly handling events such as the October 1985 disturbance.

RECOMMENDATIONS

It is recommended that a more comprehensive study be undertaken with the goal of developing a climatology of polar lows affecting Canadian waters.

ACKNOWLEDGEMENTS

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STATISTICAL SIMULATIONS OF OIL DRIFT
FOR ENVIRONMENTAL RISK ASSESSMENTS AND CONSEQUENCE STUDIES

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INTRODUCTION

Relevant information on possible drift and fate of oil spills is one of the basic requirements in environmental impact assessments related to planned or ongoing offshore petroleum activities. Such information may be obtained from statistical simulations of oil drift based on relevant environmental data - i.e. background currents and wind statistics. In regions where long time series of gridded wind data are available - such as at the Norwegian Continental Shelf - the required statistics may be obtained by simulation of a large number of spills - each with a start time chosen randomly within the available period of years of wind data.

In most cases, such simulations have been related to specific sites - where the geographic location of the oil wells, and the characteristics of the crude are known. However - in the case considered in this paper, the study concerns a new region of vast geographical extensions - to be opened for exploration in the near future - i.e. the Southern Barents Sea.

In order to cope with this situation, a new method has been developed - involving simultaneous simulations of oil drift from a large number of sites distributed evenly in the region of concern. The major aim was to provide a basis for a complete mapping of the region, from which relevant data could be extracted for any future spill site (Johansen 1988).

This paper will include a brief presentation of the basic concepts applied in this approach - and demonstrate the potentials of the method by some examples of data obtained from the simulations.

MODEL CONCEPTS

Oil drift

The simulation model is basically a traditional trajectory model, where the oil drift is computed from the vectorial sum of a permanent background current and a wind induced drift, related to the local wind by the common 3% rule. In the presence of sea ice, this rule is modified in terms of the local ice coverage:

- Oil drift is assumed to be unaffected by ice when ice coverage is below 30%.
- Oil approaching pack ice or fast ice (coverage > 90%) is assumed to be stopped at the barrier, but is allowed to resume drift when wind or current eventually turns away from the barrier

- Oil is assumed to be trapped in the drifting ice at intermediate ice coverages (30 .. 90%).

In the last case, the drift velocity of the ice field is approximated by a modified drift factor concept - 3.3% and turned 35 degree to the right of the wind (ASA 1985).

Weathering

A general environmental exposure approach is used to obtain the amount of oil associated with each spilllet at the time it eventually reaches the shoreline - reduced from the original spill size by evaporation and dissipation to the water column during the drift period. The concept is based on the assumption that 1) evaporative loss may be related to the time integral of the wind speed in the drift period, while 2) dissipative loss (oil permanently entrained in the water column) are related to the integral of the wind speed squared.

The first assumption is derived from the evaporative exposure concept identified by Stiver et. al. (1984), which relates evaporation to a dimensionless number E:

Evaporated fraction: $F = F(E)$ (1),
where $E = a t/h$,

a, the mass transfer coefficient -
approximately proportional to
wind speed,
t, evaporation time,
h, the oil film thickness.

The second assumption is derived from the first order dissipation loss concept proposed by Audunson et. al (1980):

Dissipation loss rate: $dQ/dt = - b Q$ (2),

where Q is the remaining surface oil mass,
b is the dissipation rate - assumed
proportional to wind speed squared.

Integration of (2) for the drift period gives:
 $\ln Q/Q_0 = - \text{Integral}(b dt)$

which - according to the assumption above -
is proportional to the integral
of the wind speed squared.

The application of these concepts will thus imply simple addition of wind speeds, respectively wind speed squared - at each timestep during a given drift period. By storing the actual sums obtained at the time the spilllets eventually comes to shore, data on the amount of oil stranded may be computed later - when required.

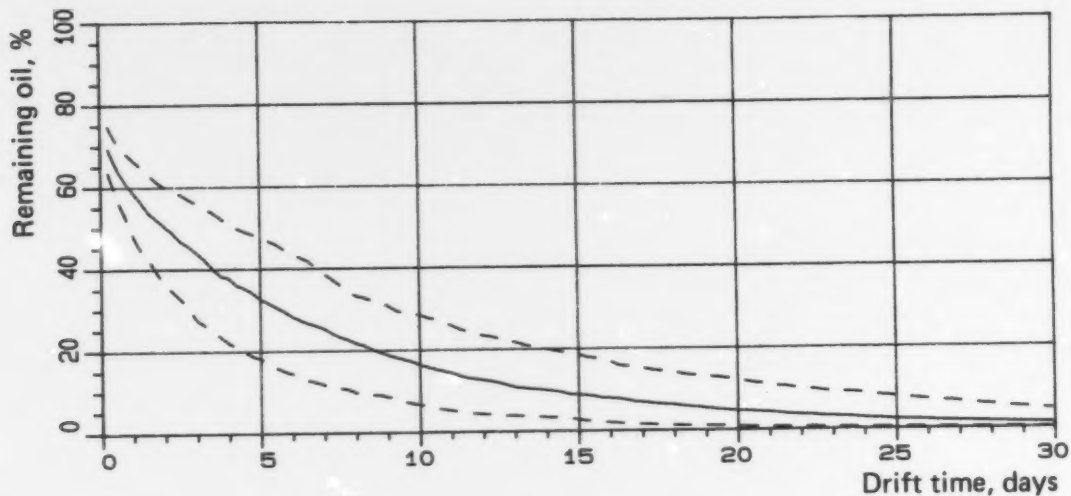


Figure 1. Remaining fraction of spilled oil after evaporation and dissipation, computed in terms of drift time. Solid line is the median value, while dotted lines represent respectively 10 and 90% percentiles. Computations based on subsequent 30 day periods in 30 years of wind data.

Figure 1 illustrates the expected variability in the remaining amount of oil under different wind situations. The graph is based on exposure parameters established at fixed time intervals within subsequent 30 day periods, sampled from the summer half year within 30 years of historical wind data. A spill rate of 100 tons/hour and a medium heavy crude (fresh oil density 850 kg/m^3) is used in this example.

Such computations may be made for any choice of spill rate or type of crude - presumed that the evaporative-loss-versus-exposure relation for that particular crude is known - and empirical data is available for the dissipation rate. The latter may - for standard wind conditions - be assumed to be related to spill size and type of oil (light or heavy oil).

In total - these concepts are found to provide a significant reduction in computational time, and to assure flexible use of the data obtained from a given run.

Environmental data

The historical wind data are provided by the Norwegian Meteorological Institute, derived from analysed pressure data and their latest hindcast wind model. The data are available in a 75×75 regular mesh, at time intervals of 6 hours in a 30 year period.

Historical data on ice coverage - stored in a 100x100 km mesh at the end of each month in within the same 30 year period - is used parallel to the wind data to enable a realistic representation of the coupling between wind and sea ice conditions.

The background current pattern is partly based on annual averaged data derived from analysis of trajectories from satellite tracked surface drifters, supplemented by general information on the prevailing currents in the region.

Simulation strategy and data storage

Trajectories are computed simultaneously for a given number of spilllets, released at evenly spaced locations in the region of concern. Thus, for each drift period - corresponding to a randomly chosen 30 day period in the available 30 years of historical wind data - a maximum number of 60 spilllets is traced by the model. In order to assure reasonable statistical convergence, one run is made to involve a repetition of this procedure for one thousand (1000) drift periods - each chosen at random within a given season of the year.

The data stored in each run is selected in order to provide a basis for relevant statistics on 1) Stranding of oil from each of the chosen spill sites in the region, used later for preparing regional maps of drift times, amounts stranded etc. - and 2) Possible conflicts between oil and vulnerable resources in the open sea. This implies:

- 1) Statistics on stranded oil is accounted for by a complete record of position and exposure parameters for each spilllet at the time trajectories eventually reach the shoreline.
- 2) Data related to drift of oil in the open sea includes an account of the number of hits and the minimum drift time from each spill site to boxes defined in a regular 15x15 km grid.

The data on stranding stored in each simulation is later used for compiling statistics on the probability distribution of drift times to shore from each chosen spill site, and more detailed information related to specific coastline sections - such as minimum drift time, probability for stranding and expected stranded amount of oil. The same data also forms the basis for regional maps, where the same set of parameters may be read out for arbitrary spill sites. These contour maps are constructed by interpolating the site specific data to a regular 15x15 km mesh.

Contour maps may also be produced from the open sea data: For any arbitrary spill site in the region, contours may be shown for the minimum drift time to - or frequency of hits in the surrounding area. Such maps may be used for evaluation of the probable area of impact related to a given spill site. Examples of both types of maps will be shown in the following.

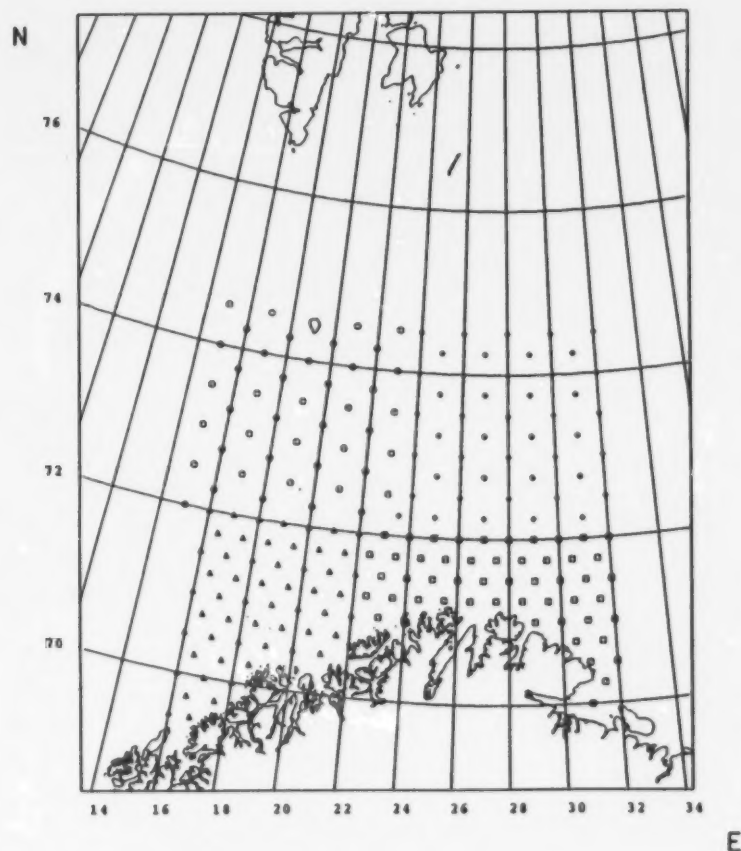


Figure 2. Distribution of the 200 spill sites in the study area. Different symbols are used for the four subregions.

APPLICATIONS

Figure 2 shows the exploration region considered in the present study, and the distribution of the spill sites used in the simulations. In order to obtain a reasonably dense coverage, the region is divided in four subregions with approximately 50 spill sites each. The total number of spill sites is thus in the order of 200.

Stranding of oil

Postprocessing of the data on stranding produces statistics for each spill site, including tables of minimum drift time and cumulative stranding probabilities for 1 day, 2 days, 5 days, and up to 30 days drift periods. Data on the geographical distribution of stranding - including probability, expected amount stranded and minimum drift time - is obtained in the same process, with reference to a chosen set of coastline sections.

Examples of regional maps based on the same set of data are given at figure 3, 4 and 5. All maps shown represents summer half year conditions, but corresponding maps are also compiled for the winter half year.

Figure 3 shows the probability for stranding of oil from arbitrary spill sites within drift periods of 30 days. According to this map - spillets originating from position 72°N , 19°E will reach the shoreline in 25% of arbitrarily chosen 30 day periods.

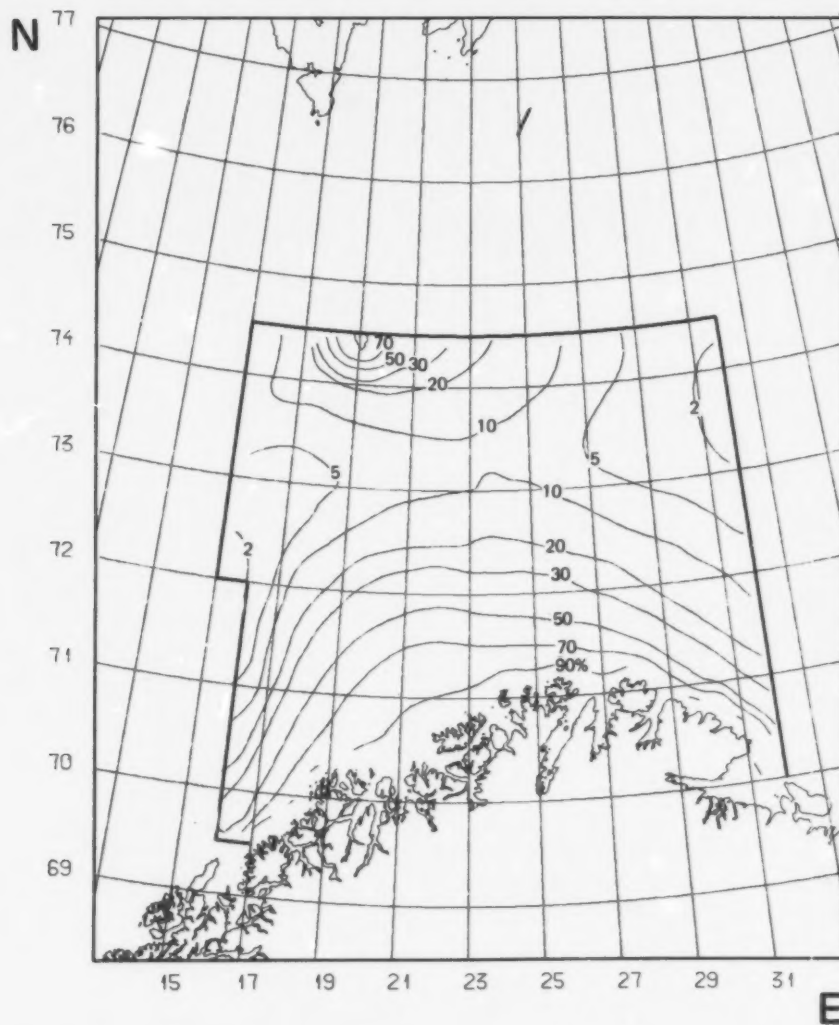


Figure 3. Probability for stranding within 30 day drift periods depending on the location of the spill site. Results based on 1000 trajectories in the summer half year.

Figure 4 shows contours for the minimum drift time to shore. A spill originating in the same location as above may - under extreme conditions reach the shoreline in a one week drift period. The probability for such an event is however small: Statistics listed for the same location reveals that stranding within less than 10 days occurs with a probability of 2%.

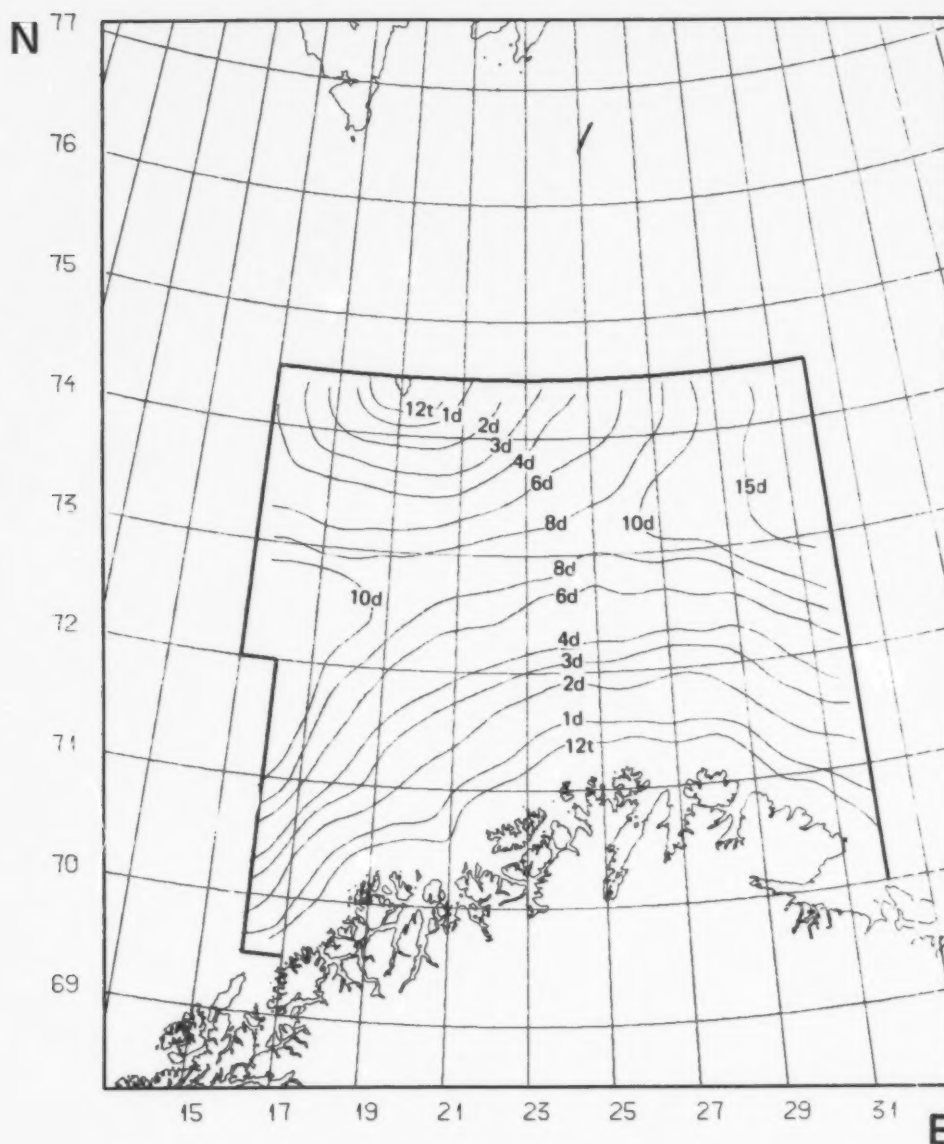


Figure 4. Minimum drift time to shore depending on the location of the spill site (summer half year).

The expected amount of stranded oil presented at figure 5 represents averaged values of the stranded mass of oil from all spills originating in specific locations. The values for each spill are compiled from the stored exposure parameters, assuming a medium crude (density 850 kg/m³), and a spill rate of 100 tons/hour. For the location used in the previous examples - the expected value is found to be rather small - i.e. slightly less than 2% of the original spilled mass.

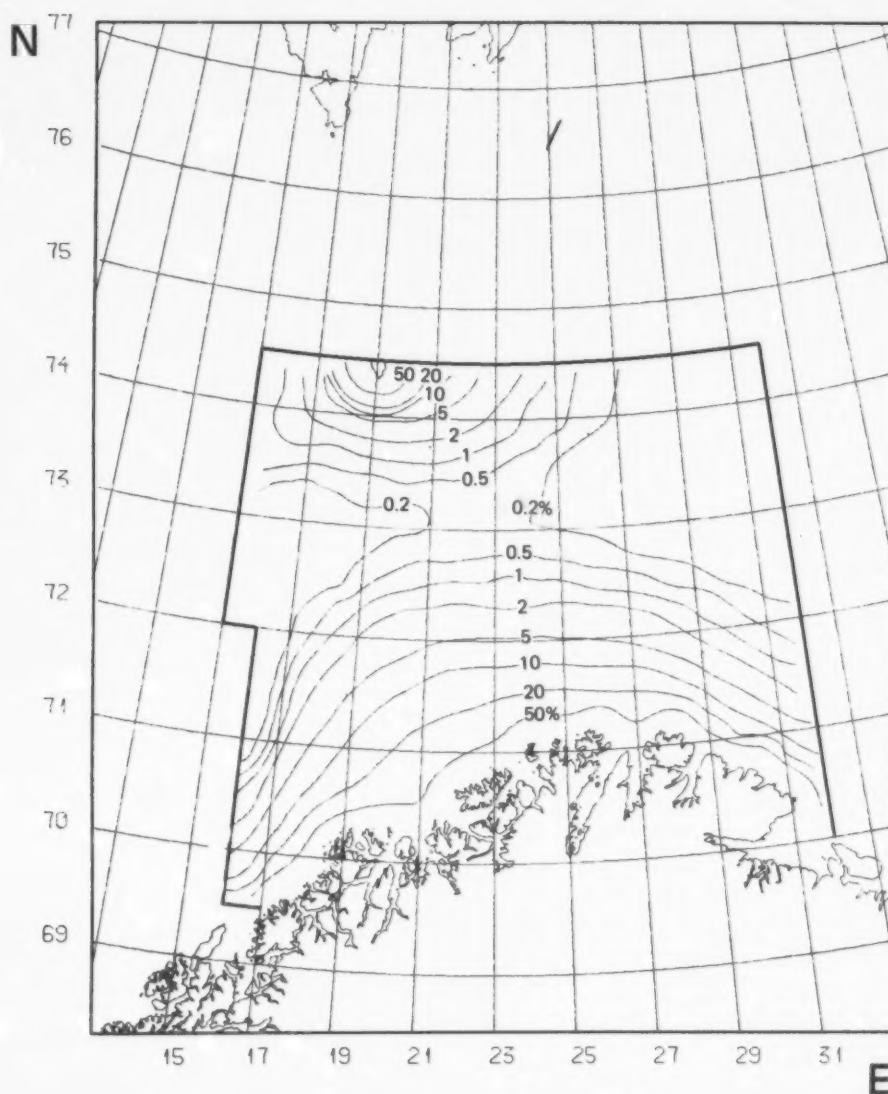


Figure 5. Expected amounts of stranded oil - expressed in percentage of spilled oil - depending on the location of the spill sites (summer half year).

Drift in open sea

The data stored for the open sea forms the basis for mapping of the infested area from all the 200 spill sites chosen in the study. In order to avoid filling several volumes with maps of different kinds, the complete dataset is made available to the other participants in the study - responsible for the more specific risk assessments. This includes a database containing all the open sea data - and software for sorting out the relevant information for any spill site in the region.

An example of maps produced from this database is presented at figure 6, which shows the expected frequency of contamination from spillets originating in position 71°N, 19°E - compiled with reference to 15x15 km grid boxes. According to this map - 10% of the trajectories originating from this location may be expected to cross a 15x15 km box located at 72°N, 16°E.

Maps of the same kind may be produced for any spill site in region of concern, based on interpolation between data from adjacent spill sites. In addition to the probability for contamination, corresponding maps may be produced for the minimum drift time from a given spill site to the surrounding waters.

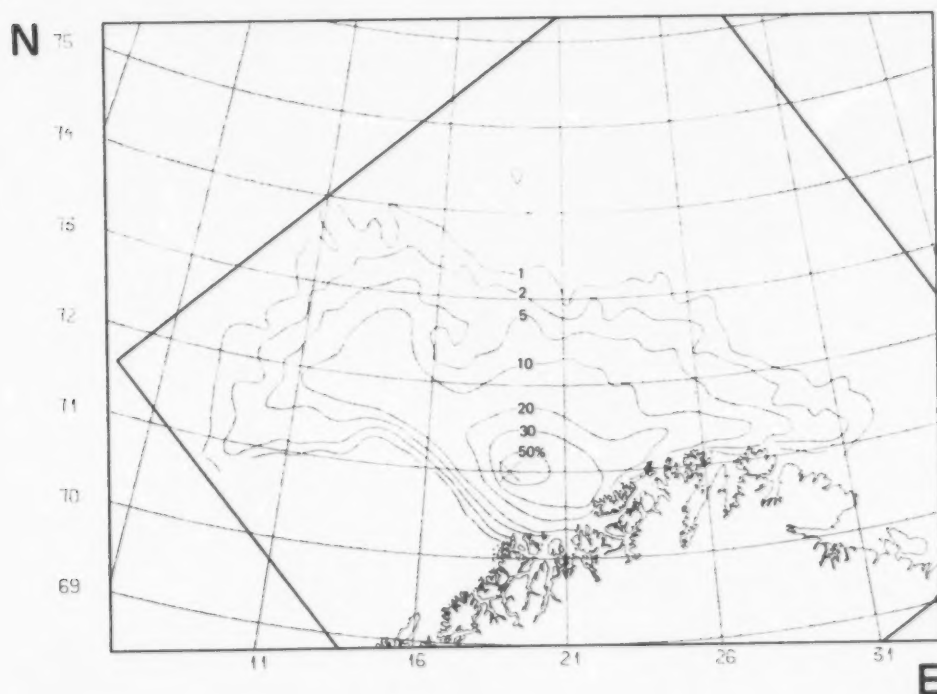


Figure 6. Probability for contamination of locations in the open sea from spillets released in a specified spill site (marked with X on the map).

Sea ice

The presence of sea ice is taken into account in the computations of the oil drift by the use of historical data on ice coverage in parallel to the historical wind data. However - the data obtained in the simulations on the conflict between oil and ice is found to be too scarce to form a basis for relevant statistics. This is partly due the fact that the ice border in general is far north of the region where spills are considered to take place. The probability for oil contamination of these northern regions are low in general, and the combined probability for ice and oil being present simultaneously seems to be too small to be determined with reasonable significance - even from the 1000 spill cases considered in this study.

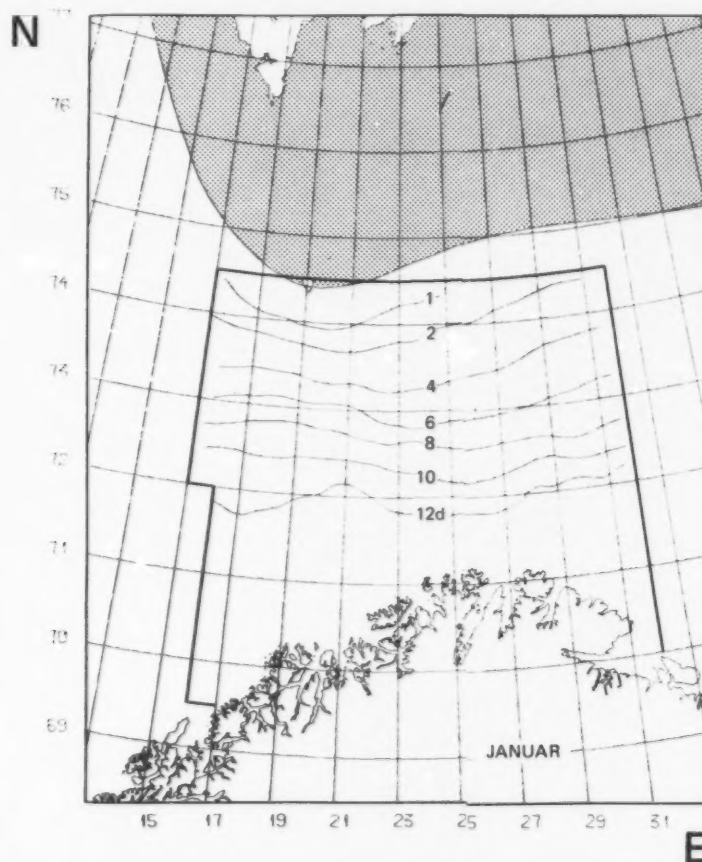


Figure 7. Minimum drift time to the expected ice border in January - depending on the location of the spill sites. The expected extension of the ice infested region is based on 30 years of ice coverage data, specified at the end of each month.

As a replacement for such statistics, the expected location of the ice border is determined at the end of each month from the 30 years of ice coverage data. The minimum drift times to these borders are further more assumed to be independent of the actual month, but only dependent on the season of the year (summer- and winter half year). By combining the open sea drift data from the 200 spill sites in these two seasons, with the monthly median ice borders, maps as shown at figure 7 are obtained.

These maps are primarily designed as a tool for oil spill contingency planning: If the minimum drift time to the expected ice border is less than a couple of days, or the expected ice border interferes with the planned drilling location, conventional mechanical oil spill combat equipment may not serve the purpose, and special equipment suitable for ice infested regions should be considered.

CONCLUSIONS

The new method for statistical oil drift simulations, which is presented in this paper, is designed to serve as input for environmental risk assessments and oil spill contingency planning in the large Barents Sea South region of the Norwegian Continental Shelf - to be opened for exploration drilling in the near future.

The primary output from this method includes regional maps - relating drift times to shore and stranding probabilities to the location of potential spill sites. In addition, statistical data are compiled for each of the chosen spill sites, in terms of tables on the distribution of drift times to shore, probability for stranding, and expected amount of oil stranded with respect to specific coastline sections. Data for oil drift in the open sea from each of the spill sites - and software for accessing these data - are also made available to other participants in the environmental risk assessment study.

An implementation of the model for the Norwegian Sea and the North Sea region has been made recently - to be applied in ongoing studies related to new offshore exploration areas at the Norwegian Continental Shelf. This model may also be used in other offshore areas - provided that the required historical data (wind, ice coverage) are available, and the prevailing ocean current pattern is reasonably well known.

ACKNOWLEDGEMENTS

The development of this model, as well as the application which forms the basis for the examples shown in this paper - has been funded by the Norwegian Oil and Energy Department under the AKUP-program, related to the planned opening of the Barents Sea South region. Inputs from the many other participating research groups in this program have been of great use in the final design of the model.

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Oil Spill Trajectory Analysis on the Alaskan Outer Continental Shelf

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INTRODUCTION

Oil spills are a major concern associated with offshore oil development in all Outer Continental Shelf (OCS) lease areas. The U.S. Minerals Management Service (MMS) uses the Oil Spill Risk Analysis (OSRA) model to estimate risks of spills from production and transportation of oil projected in Federal waters of the OCS. The OSRA is able to make use of a number of site- and process-specific circulation/trajectory models for the many OCS regions offshore Alaska, shown in Figure 1.

The model, using an efficient coordinate transformation procedure to incorporate trajectory information provided by external circulation models, traces hypothetical oil spills through a matrix of grid cells. The grid matrix also stores the locations of biological and recreational resources that may be vulnerable to oil, the representation of the coastline in the study area, and the potential locations of offshore spill sites such as platforms and pipelines or tanker routes. Given that different trajectory algorithms are necessary to model the many OCS lease areas under study, the use of a common tracking model enhances consistency in the MMS' overall approach to risk assessment.

Information will be presented on past analyses of several regions within the Beaufort, Chukchi, and Bering Seas and Cook Inlet/Shelikof Strait.

The circulation/trajectory models used will be identified with emphasis on their use with OSRA to provide quantitative information for environmental impact assessment.

CHARACTERIZATION OF THE MODEL

OSRA, described in detail in Smith et al., 1982, is not designed to simulate a particular spill event, but rather to model a series of randomly occurring spill events from various potential spill sites. A stochastic approach is appropriate in order to estimate contact probabilities to numerous coastal resources over the 15- to 25-year lifetimes of OCS leases. This requires that many trajectories are simulated from numerous spill launch sites varying in time and location throughout the study area. Also, a wide array of seasonal surface current and wind conditions in each region is needed to represent the variability and physical characteristics of the area under study. The resulting trajectories will in turn allow the calculation of statistics of potential contact.

It is important to note that OSRA itself does not calculate winds, currents, or trajectories for modeling in the Alaska region. An interagency agreement between MMS and NOAA has provided financial and technical support in the development and procurements of trajectory models used as inputs to the OSRA process.

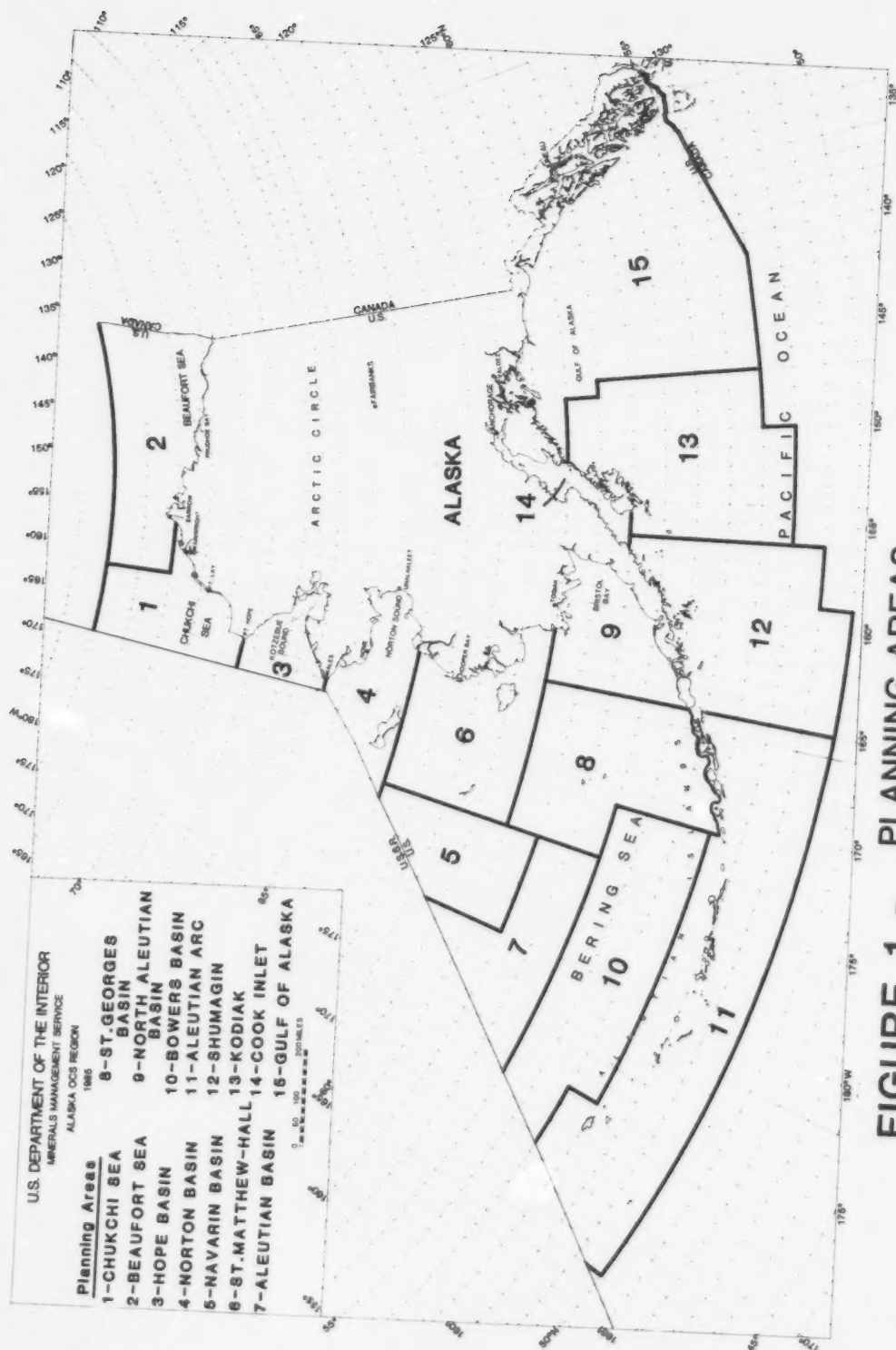


**FIGURE 1 - PLANNING AREAS
ALASKA OCS REGION**

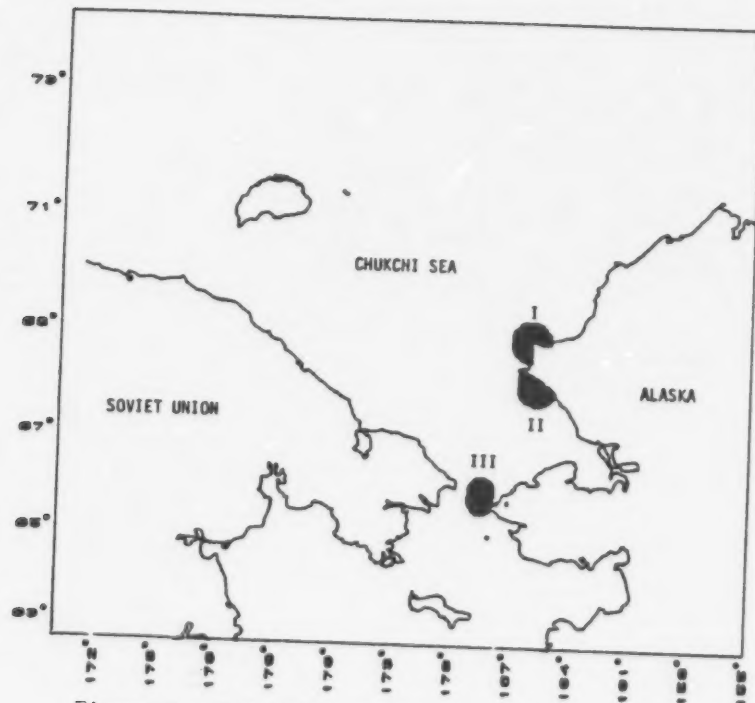


Figure 2 - Modeled location of sea bird colonies in the Chukchi Sea.

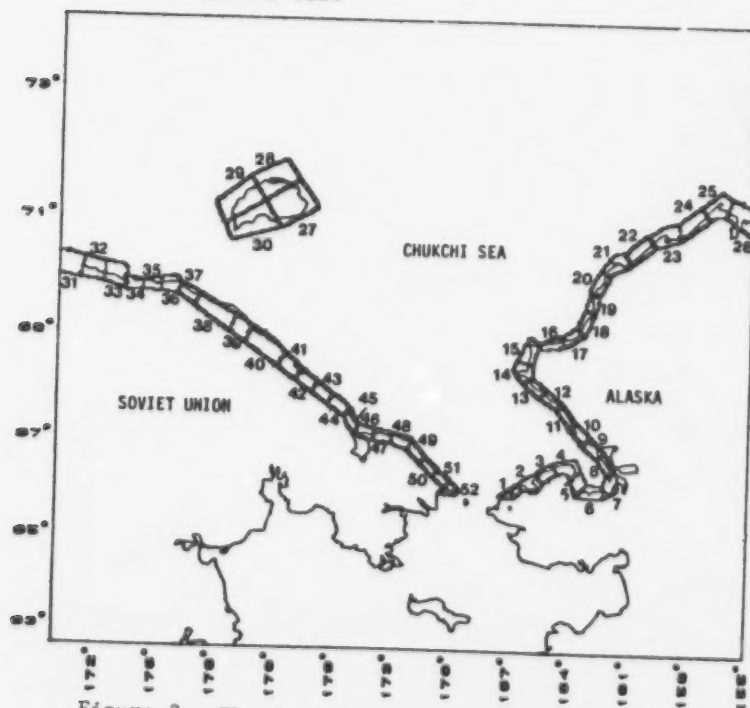
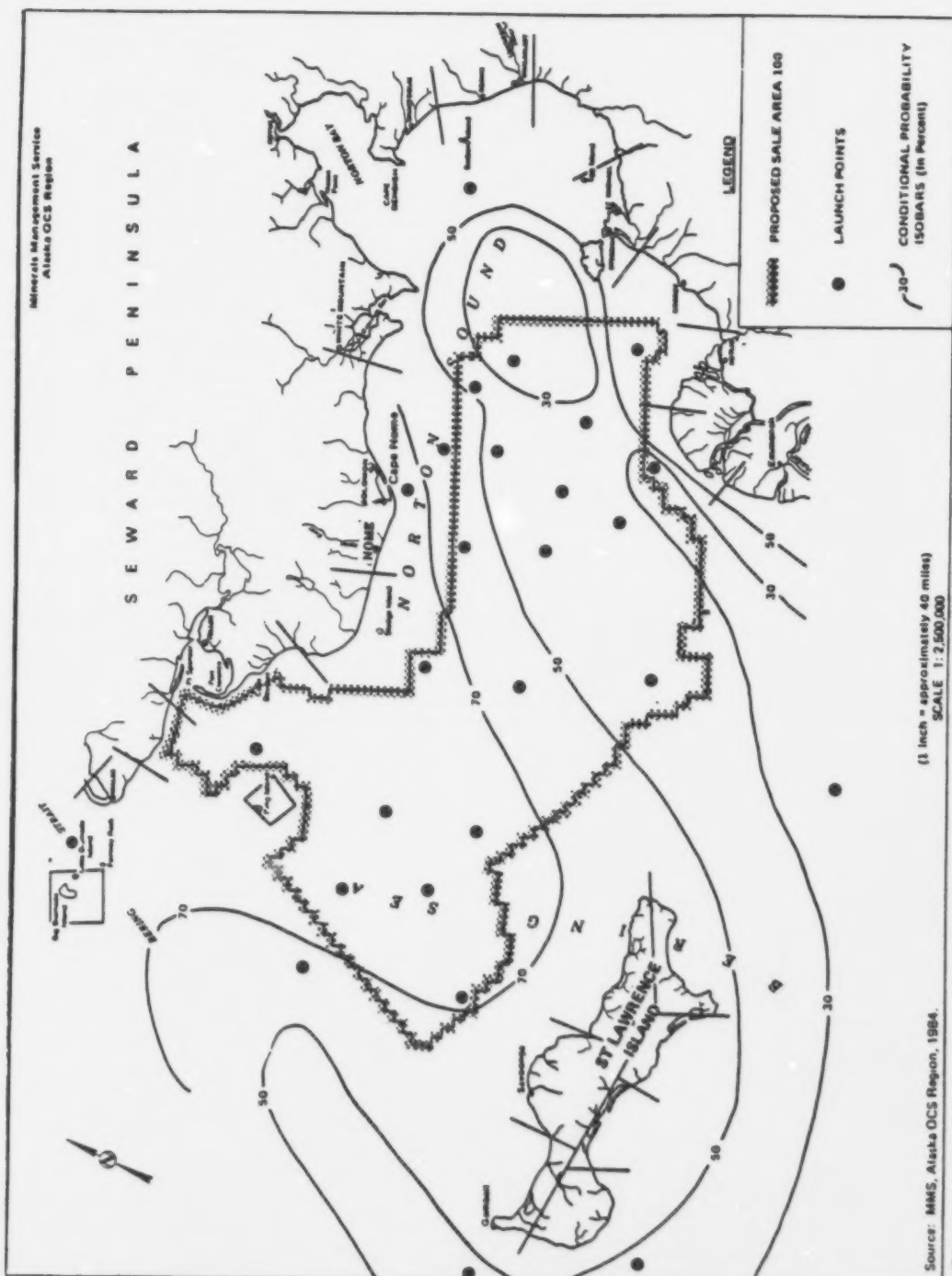


Figure 3 - The division of the coastline into 52 land segments of approximately equal lengths.



Representations of Physical Data

OSRA employs a Cartesian coordinate system superimposed over a base map of the area under study for a given analysis. All stored data are referenced to this grid system, and it is used for all internal calculations. The base map must be large enough so that all coastal resources likely to be affected by the proposed lease action are included. This involves a tradeoff, with grid resolution decreasing as the area modeled is expanded. Typical resolution off Alaska is on the order of 2 to 4 km sq. per grid cell.

Spatial data, including the presence of land or resources, are digitized from standard Mercator or UTM projections and stored in matrices of grid cells for rapid retrieval and access. The model stores indicators of the locations of up to 32 representations of such resources as fishing areas, shorebird foraging areas, or endangered species habitats. An example of modeled seabird colonies in the Chukchi Sea is presented in Figure 2. Since many wildlife populations display seasonal migration, the model accounts for monthly presence or absence of the resource in the study area. For example, spawning areas may only be vulnerable to spilled oil during certain months of the year. Therefore, contacts with trajectories would only be counted for those months.

For simulated spills that hit land, the model allows the coastline to be divided into segments, as in Figure 3. When a trajectory contacts a grid cell containing land, a check is made to store the number of the land segment contacted. This provides analysts with an overall spatial distribution of spill contacts to shore, enabling modeling of such resources as mud flats or marshes. In addition, since the trajectory models used are not applicable to bays or estuaries, this feature will at least provide estimates of spills which would have entered these waters. For this reason, bay entrances are treated as part of the shoreline, with an associated "land" segment.

The model analyzes spill trajectories from a set of potential launch points chosen to represent proposed OCS platforms, pipelines or tanker routes (see Figure 4). A single launch point may represent a group of proposed lease tracts, but additional points are often needed to represent transportation routes to shore.

OIL SPILL MOVEMENT

Hypothetical oil spill trajectories obtained from circulation/trajectory models are processed through the tracking/probability routines of OSRA. Transformation functions are developed to convert the trajectory model grid coordinates to standard latitude/longitude and then to Mercator coordinates. The Mercator coordinates are then converted to OSRA grid coordinates. If the grids are defined on the same projection, the transformation is linear. Nonlinear transformations for matching grids defined on different projections have also been developed. For further information on the procedure, see Samuels, et al., 1983.

OSRA uses trajectory results to simulate oil spill movement as a series of displacements over finite time intervals (specified by the trajectory model used, usually 3 hours). The spill's center of mass is moved in a straight line between its initial and updated grid coordinates, as illustrated in Figure 5. Any cells through which a spill passes are checked for the presence of resources. This tracking continues until a given time has elapsed (usually 30 days), the spill hits land, or leaves the study area. Upon first contact with a resource, the simulated age of the spill is recorded.

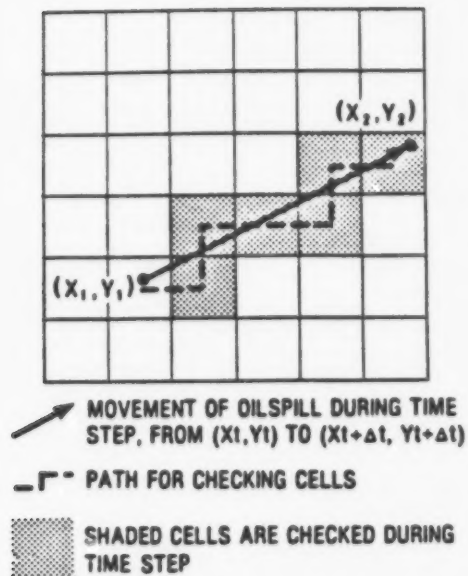


FIGURE 5—Movement of a hypothetical oilspill through the model's grid system during one time step.

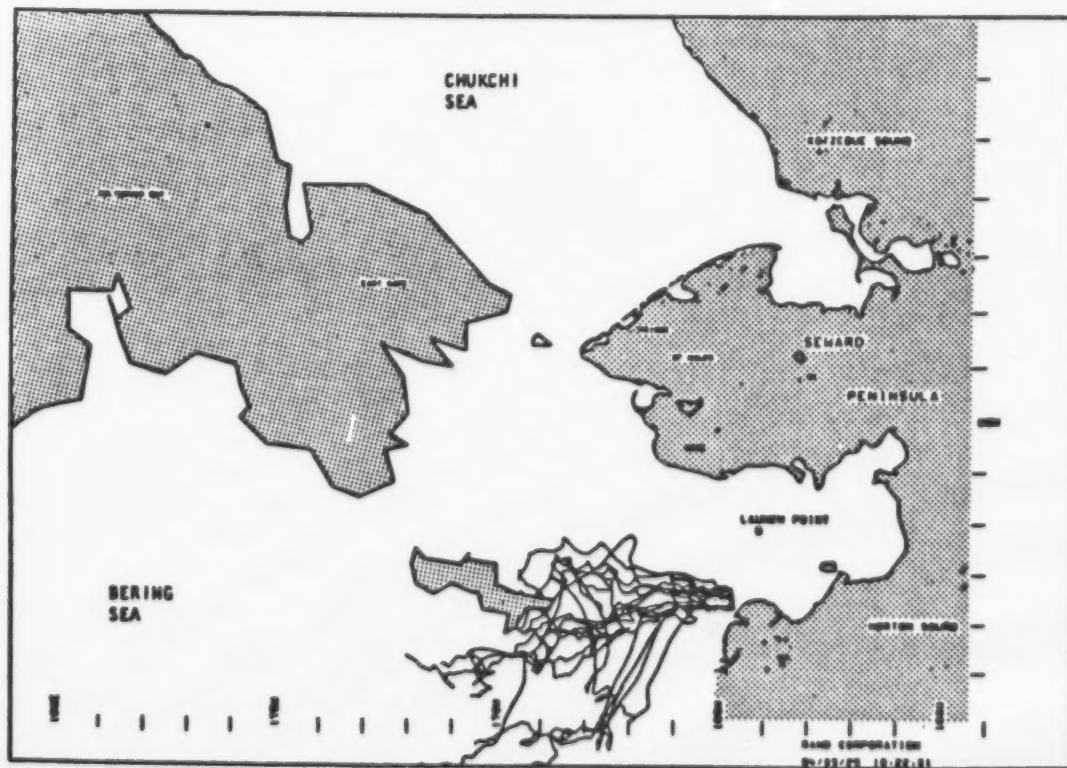


Figure 6 Thirty-day displacements of oil spill trajectories launched from a hypothetical spill site under 25 stochastic weather scenarios during the winter oceanic period. (Source: The Rand Corporation, Santa Monica, CA, 1984).

Trajectory Models

Past analyses in the Beaufort, Chukchi, and Bering Seas have incorporated the Rand Corporation's three-dimensional model for estuaries and coastal seas (Liu and Leendertse, 1979 and 1981). The basic model is formulated on a finite difference grid, according to the equations of motion for water and ice, continuity, state, the balance of mass, heat, salt, pollutant, and energy. This allows for the computation of the vertical density structure and baroclinic circulation. Local wind stress was modeled using a method called the unit response function. Response functions were generated by the differences in the currents in the three-dimensional field with and without the wind stress under identical tidal conditions. Under ice-free conditions, the response function (including a storm-tracking feature), together with the local residual current, was used to compute the movement of oil. Figure 6 illustrates examples of trajectories launched in Norton Sound under stochastic winter weather scenarios. Oil was also modeled in ice conditions as described in Liu and Leendertse, 1981. Oil spill trajectories in Cook Inlet/Shelikof Strait have been simulated using a model developed by Dames and Moore (Schleuter and Rauw, 1980). Wind fields were defined by spatially dependent flow patterns and six intensity factors and correlated to the 22 baric weather patterns developed by Putnins (1966). Surface currents were divided into a time-dependent tidal flow and a seasonal constant net surface circulation. The spill's center of mass was assumed to move in the same direction as the wind vector, with 3% of the wind speed imparted to the slick.

Further information on less frequently used trajectory models can be found in Samuels et al., 1983.

Present Efforts

Applied Science Associates (ASA) is now under contract with MMS (through NOAA) to provide OSRA with spill trajectories in all Alaskan coastal waters. Runs of the ASA model are underway for risk analyses in the Navarin and St. George Basins. Components of the coastal sea model system include models to predict the three dimensional circulation dynamics driven by tide, wind and density-induced forcing, wind speed and direction, ice dynamics, and oil spill fate and trajectories (Spaulding, et al., 1988).

ASA has performed a series of verification studies addressing the influence of specification of open boundary conditions, grid size, bottom friction coefficient, and wind-forcing representation (Spaulding, et al., 1987); and circulation in response to semi-diurnal and diurnal tidal forcing (Isaji, et al., 1988). As shown in Figure 7, sample trajectories launched in the Navarin Basin in winter reflect the variability of the wind. Winter winds from the northeast and the presence of sea ice on the Bering Sea shelf both favor southwesterly trajectories (Spaulding, et al., 1988).

IMPACT ANALYSIS

Conditional Risk Calculation

The numbers of contacts to resources and land segments from total number of trajectories launched from each point are tallied and stored on disk files. These files are used to calculate the conditional probabilities that, given a spill at a certain launch point, certain resources will be contacted within a specified period of time. With sufficient simulations from each launch point, the statistical behavior of the trial spills will approximate the statistical behavior of spills integrated over all possible combinations of release times, winds, and currents.

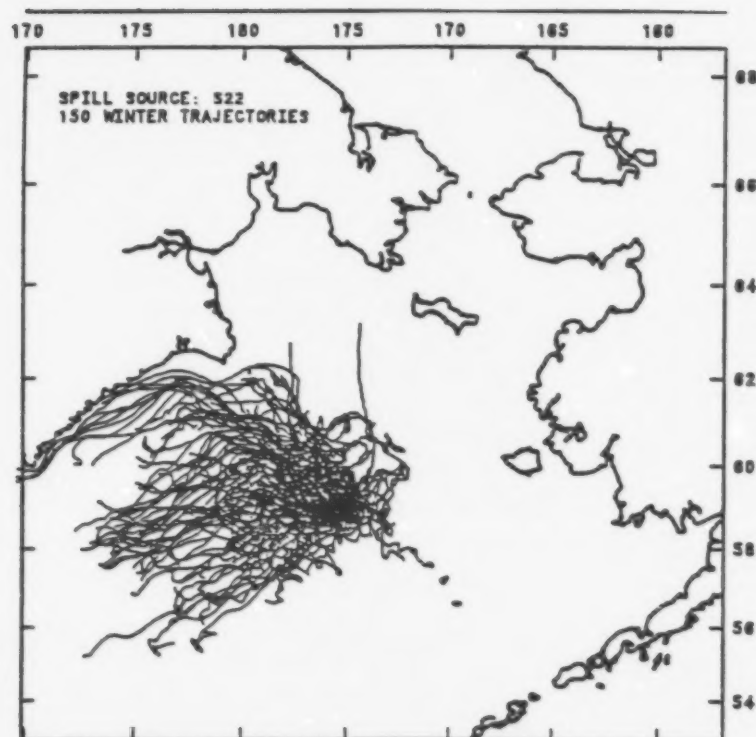


Figure 7 - Oil spill trajectories for launch point S22, Applied Science Associates Navarin Basin Oil Spill Trajectory Model. (Spaulding et al., 1988)

Table 1 -- Probabilities (expressed as percent chance) that an oilspill starting at a particular location will contact a certain target within 30 days. Spills launched during the ice-free season.

Target	Hypothetical Spill Location																			
	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20
Land	62	46	62	31	31	35	54	38	27	31	4	n	n	4	n	n	n	n	n	n
COAST. BIRD CONC. A	n	n	n	n	n	n	n	n	n	n	4	n	n	n	n	n	n	n	n	n
COAST. BIRD CONC. B	n	8	58	**	**	73	12	n	n	n	n	n	n	4	n	n	n	n	n	n
COAST. WIRD CONC. C	73	**	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n
GRAY WHALE FEEDING	n	n	n	n	n	n	n	81	**	**	27	**	8	n	n	n	n	n	n	n
BOWHEAD WIGR. A	65	**	69	77	19	4	n	n	n	n	n	n	n	15	n	8	n	n	n	n
BOWHEAD WIGR. B	4	4	12	62	77	62	65	**	**	56	4	38	35	**	n	19	n	n	n	n
BOWHEAD WIGR. C	n	n	n	n	n	n	n	n	15	**	**	4	n	n	n	n	n	n	n	n
SEABIRD COLONY I	n	n	n	n	n	n	n	n	96	31	n	23	4	n	n	n	n	n	n	n
SEABIRD COLONY II	n	n	n	n	n	n	n	n	8	**	4	n	n	n	n	n	n	n	n	n
SEABIRD COLONY III	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n
SUBSISTENCE AREA A	31	**	**	8	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n
SUBSISTENCE AREA B	n	4	19	**	12	n	n	n	n	n	n	n	n	4	n	n	n	n	n	n
SUBSISTENCE AREA C	n	n	n	n	n	n	n	n	**	34	n	n	4	n	n	n	n	n	n	n
SUBSISTENCE AREA D	n	n	n	n	n	n	n	n	8	**	4	n	n	n	n	n	n	n	n	n
SEA SEGMENT 1	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n
SEA SEGMENT 2	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n
SEA SEGMENT 3	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n
SEA SEGMENT 4	n	n	n	n	n	n	n	n	n	n	n	n	n	n	19	n	12	n	n	n
SEA SEGMENT 5	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	4	54	n	n	n
SEA SEGMENT 6	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	4	n	15	n	n
SEA SEGMENT 7	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	38	n	4
SEA SEGMENT 8	4	n	n	n	n	n	n	n	n	n	n	n	n	n	n	4	n	n	n	n
SEA SEGMENT 9	4	12	n	n	n	n	n	n	n	n	n	n	n	n	n	4	n	n	n	n
SEA SEGMENT 10	12	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n

Note: ** = Greater than 99.5 percent; n = less than 0.5 percent.

Conditional probabilities are reported for each launch point for all resources, as shown in Table 1. This information is also broken down into contact probabilities for the specific seasons modeled by the trajectory analysis. It should be noted that such seasonal statistics are calculated from a subset of the total simulations, and therefore may be less reliable than the conditional probabilities based on all seasons combined.

In like manner, conditional probabilities are calculated for each land segment. Since spills are modeled as a point with no dimension, analysts should assume that contact anywhere in a given land segment would affect the entire (and possibly neighboring) land segment. This will implicitly account somewhat for the spreading of actual slicks along shore.

All conditional probabilities are stored in matrix form for further use in OSRA's subsequent calculation of the likelihood of spill occurrence and contact. Further information on this aspect of the model can be found in Smith, et al., 1982.

Use of Conditional Probabilities

Despite assuming oil spills have occurred, the OSRA conditionals are not a "worst case analysis" for purposes of impact assessment in the EIS. Rather, the conditional probabilities are generated from trajectories that represent climatology or average conditions over the projected lease lifetimes. For example, storm track submodels may be sampled, but only in accordance with the estimated historical frequency of storms within a given area. In this way analysts may use the conditional probabilities as a model of what is most likely to happen in general if oil is spilled. Figure 4 provides an example of graphics used in the EIS and based on OSRA conditional probabilities.

Conditionals are used to compare relative risks from alternative groups of lease tracts and different scenarios for transportation of OCS oil to shore. They provide an indication of the tracts most likely to result in contact of oil to shore (or to resources), if a spill in fact occurs. This information may also be used in planning optimal locations of limited amounts of spill containment and cleanup equipment, as well as in estimating the average time spills would take to contact the shoreline.

Analysts are cautioned that, in terms of conclusions of impact assessment sections in the EIS, conditional probabilities should only be used when the likelihood of oil spill occurrence from each launch site is also factored into the analysis.

ACKNOWLEDGMENTS

The contribution of Ravenna K. Westphal in the preparation of this paper is gratefully acknowledged by the author.

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The Use of Remote Sensing in the Determination of Dispersant Effectiveness.

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ABSTRACT:

There have been several experiments in recent years designed to measure dispersant effectiveness in an open ocean environment. These have been conducted in a number of countries including England, Norway, France, the United States and Canada. In recent years, many of these experiments have included a remote sensing program. A variety of sensors have been used, including side looking radar, photography, passive and active microwave as well as Infrared (IR) and Ultraviolet (UV) sensors. In most of the Canadian experiments, IR and UV sensors have been used. As a result of a recent experiment conducted in 1986 in the Canadian Beaufort, a number of issues have been identified concerning the use of UV/IR equipment to measure dispersant effectiveness. These include the formation of emulsion balls, which appear thermally active, the present of a thermally suppressed region, and the variability of ambient solar radiation. These factors will be discussed and their impact of the measurement of dispersant effectiveness will be considered.

It is concluded that until the nature of emulsion balls and their formation criteria can be determined and a remote sensing method of oil thickness measurements can be developed, that it is not possible, with any degree of precision, to measure dispersant effectiveness using UV/IR sensors alone.

1. Introduction

When large quantities of oil are spilled on water, the resulting slick covers a vast area. Since a typical slick thickness is less than 100 microns, one cubic meter of oil covers more than 10,000 square meters and has a radius of greater than 50 meters. Experience has shown that oil of this thickness is very difficult to see from the sea surface, and hence airborne observations are used in most oil spill situations. While the human observer can easily see patches of oil, it is possible to confuse oil with seaweed, bottom features or

even cloud shadows. Hence, there has been a considerable effort devoted to the development of various sensing systems for the detection of oil on the water surface.

2. Previous Studies

The most common and successful system involves detectors operating in the near ultraviolet (3-5 micron) and the thermal infrared (8-14 micron) regions. The bands are selected as those regions of minimal atmospheric absorption. These sensors are extensions of the visual observation techniques to parts of the spectrum beyond the capability of the human eye. The ultraviolet sensors are effective in detecting the presence of hydrocarbons on the water due to the increased reflectivity of the surface (Catoe, 1973). Typical ultraviolet instruments use a standard video camera (either vidicon or CCD device), with a high sensitivity in the ultraviolet, a band pass filter with transmission in the ultraviolet, and a polarizing filter to reduce the effects of sun glitter. The contrast obtained between oil and water is small. This imaging technique allows the determination of the presence of hydrocarbons on the surface, but cannot penetrate the surface.

Since much of the area of a oil slick consists of thin sheen with a thickness of a few microns, it is desirable to have a second sensor that can differentiate between thick (>100micron) oil and sheen. The most widely used system for this purpose is a thermal infrared detector operating in the 8-14 micron band. The infrared sensor operation depends on the fact that the apparent temperature of the thicker oil (>100 microns) is different from the surrounding water. There are a number of competitive effects such as solar energy absorption of incident radiation, evaporation, and the lower thermal conductivity of the oil compared to the water that contribute to the generation of a real temperature difference between the oil and water. These factors are due to the differences in the physical and chemical properties of oil and water. The differences in emissivity between water and oil also are a component that generates an apparent thermal contrast.

Experience has shown that by using a high sensitivity IR sensor, it is possible to detect the present of the thicker components of the slick from the air. There are two types of imaging systems, a line scanner which generates line imagery perpendicular to the flight line using a rotating mirror. A two dimensional image is generated by repetitive scanning, using the motion of the aircraft to generate the second dimension. This line scanning system requires a unique set of processing equipment and algorithms in order to interpret the data, since the scale in one dimension is determined by the aircraft forward speed. The same line scanning system can be supplied with an ultraviolet detector, and hence both presence of oil and the location of the thick oil can be detected using the same instrument package.

A second infrared type system uses a bi-directional scanning and produces a TV-raster image. These images can be recorded using standard television recording equipment, and can be analyzed using readily available video image processing techniques. Video IR cameras are easy to couple with a UV sensor to provide a integrated sensing package.

3. Description of Current Systems

A system that has been used for a number of dispersant trials in Canada, uses a combination of infrared and ultraviolet sensors, both of which produce standard NTSC video images. These signals are viewed on a monitor, and recorded on a standard industrial video recorder in the remote sensing aircraft. The data from the tapes are

subsequently corrected for geometric effects, and the resulting images are analyzed in terms of slick areas and positions (Goodman and Brown, 1987).

With the development of small, powerful microcomputers, it is now possible to do the image analysis in real time on-board the aircraft and thus monitor the progress of the slick from the air. During a recent experiment designed to study dispersant effectiveness under Arctic conditions, such a system was used. The design and implementation of the experiment is discussed by Swiss et al (1987). The remote sensing system, with the associated image processor was used to measure the slick areas in real time. Since the system used was a single channel unit, most the recorded slick features were of the thermally active areas as detected by the infrared imaging system. Four slicks were studied, three of which were treated with dispersants while the fourth was used as a control. A simple analysis of the results indicated that the slick area for the control slick reduced more rapidly than the areas of the treated slicks. This would indicate that the application of dispersants hindered the dispersion of the oil. Since observers in the air and on the surface vessels saw physical evidence of dispersion in the form of dispersed oil clouds in the water, there was obviously some problem with the interpretation of the remote sensing data.

4. Limitations of Present Operational Systems

There are a number of possibilities to explain the incongruity of the results. Some of these are in the nature of the sensing systems, some in the method of data interpretation and some in the nature of the various interactions between the oil and water on the ocean surface.

4.1 Analysis Methodology

In the analysis, it is assumed that the thickness of the oil as a function of time is the same for both the control and treated slicks. The thickness can be estimated from equations developed by Fay (1969,1971). Since the period during which the sensing occurred was long after the slicks had been applied, the spreading is in the surface tension-viscous phase. In this phase, the critical parameters are the surface tension of the oil-water interface and the effects of horizontal diffusion which are not included in Fay's model. When dispersants are applied to an oil slick, there is a reduction in interfacial tension of an order of magnitude. This would mean that the dispersant treated oil would spread more rapidly than the untreated oil, and hence on the average the slick thickness would be less. This has been found in previous experiments (Goodman et al 1981, Goodman et al 1984), but only the total area of the slick was measured, which includes the very thin sheen. The effect of this would be to underestimate the amount of oil in the control slick.

Since there is no available technology to measure the thickness of oil, either from the water surface or the air, it is not possible to undertake a study to confirm this theory.

4.2 Thickness Measurements from Surface

The direct measurement of the thickness of the oil film is difficult under actual field conditions. A mechanical sampling system developed for the 1983 Halifax trials (Swiss and Gill, 1984) by Belore (1982) is subject to very large errors. Laboratory experiments have shown errors as large as an order of magnitude due to the interaction of the sampler with the slick. A typical set of data is shown in Table 1.

Sorbent Type and Treatment	Relative Error
3x3" square Graboil	45.4
4x4" square Graboil	32.7
5x5" square Graboil	-11.4
5.75" diam. Graboil	-4.8
4" diam. Graboil	23.3
3x3" square 3M sorbent	43.6
5.75" diam. 3m sorbent	30.9
Sorbent with Foil (and sampler)	
3x3" square Graboil	-17.2
4x4" square Graboil	5.5
5x5" square Graboil	-37.2
5.75" diam. Graboil	-22.0
4" diam. Graboil	-22.8
5.75" diam. 3M sorbent (with sampler)	-19.7

These are preliminary results from for Environmental Canada test data. Details will be published in a future Environment Canada publication.

There is a tendency for the person undertaking the sample collection to select the more obvious thick oil patches, so as to obtain a "good" sample. This lack of a systematic approach and the inability to sample in a spatially predetermined manner results in a over estimation of slick thickness.

Using thickness values obtained by this technique would lead to errors in the measurement of dispersant effectiveness that would cover the range of results reported by other workers (Goodman et al, 1987)

4.3. IR image interpretation

In the interpretation of this imagery, it is assumed that the oil that is thermally active is thick oil. Observations from the survey vessels during the Beaufort spill indicate the presence of emulsion balls on the water surface and no raw crude oil. These emulsion balls are a tertiary emulsion, that is water-in-oil-in-water and are stabilized by the presence of a mono-layer of surfactant on the water surface (Tang, 1987). The structure in shown in Figure 1.

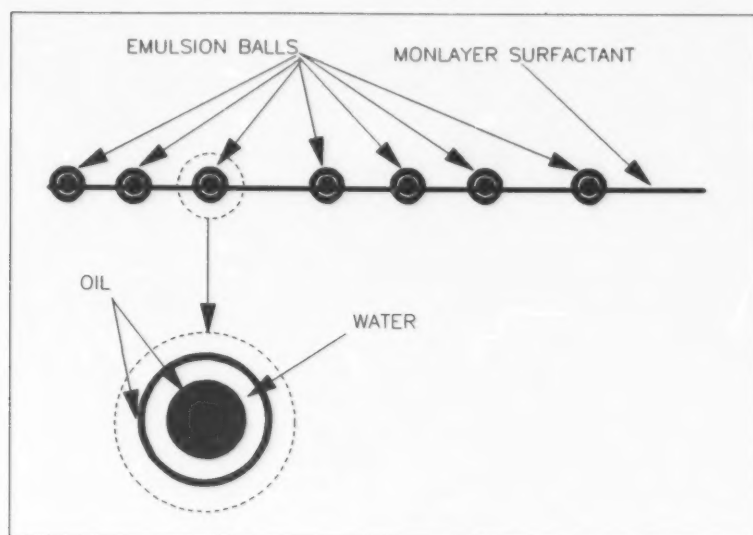


Figure 1. Structure of Emulsion Balls

Attempts to sample this material were unsuccessful since the unstable emulsion was destroyed in the collection process. Many other workers have observed this effect in field trial situations, but to date these have not been simulated in smaller scale experiments. In order to form the emulsion, some form of nucleating agent is required. These may not be present in sufficient density in smaller scale experiments. It is likely that this emulsion material would be thermally active and could be confused with crude oil. The oil to water ratio in these emulsions is about 1 to 4.

In the infrared images, there is a region of temperature suppressed sea surface. (Figure 2)

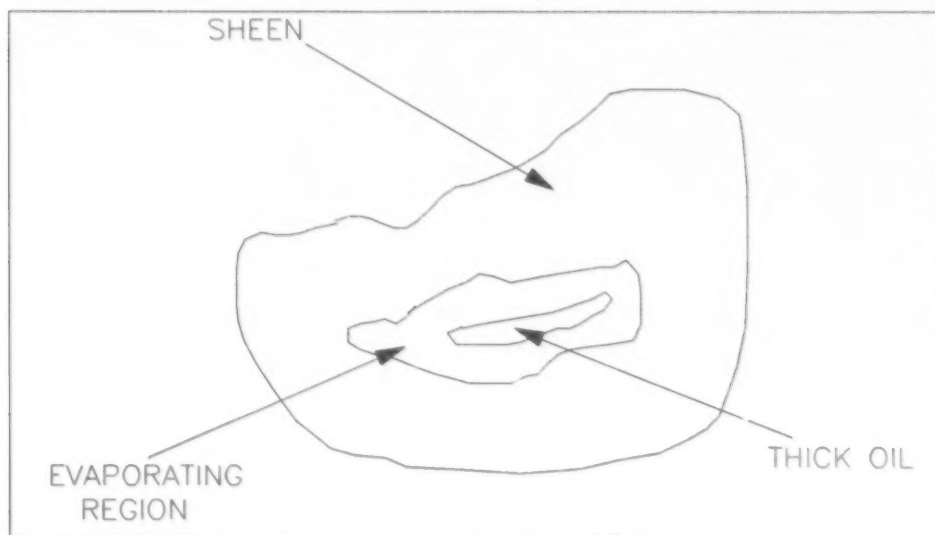
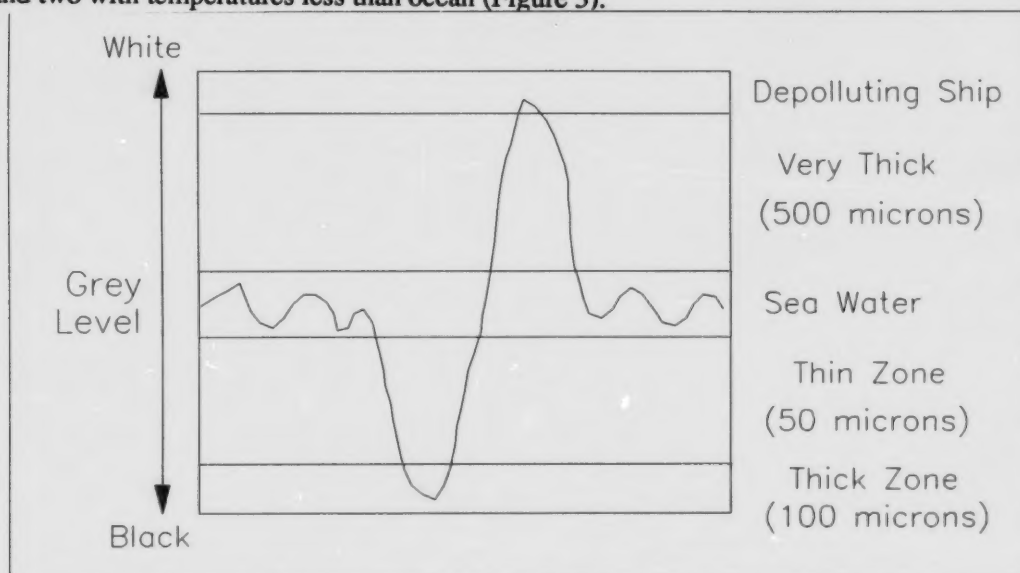


Figure 2. Regions of a typical slick

The thermally negative region is probably a thin layer of oil, in which the dominant energy loss is due to evaporation, thus lowering the temperature.

An alternate interpretation of IR imagery is given by LeGuen et al (1987). They identify three levels of infrared returns, one with a temperature greater than the surrounding water and two with temperatures less than ocean (Figure 3).



The warmer oil is assumed to be very thick material (>500 microns) and can be either oil or an emulsion (chocolate mousse). The region with the slightly lower temperature than the water is postulated to be thin oil (<50 microns) and the region of lowest temperature is assumed to be thicker oil (100-300 microns). These assignments are based on expected values of radiation and have not been confirmed by observations at the ocean surface.

If the oil that is being detected at the surface is not crude oil, but rather an emulsion, then the emission properties in the infrared could be very different. No experiments have been undertaken under controlled conditions on this material. Changes in emissivity between oil and water might account for the detection of the emulsion, rather than a real temperature difference in the oil.

4.4. Process Issues

There are a number of process issues at the ocean surface that cause difficulties in the interpretation of the infrared images. The mechanism for the formation of emulsion balls is not well understood and the criteria for formation has not been well characterized. These emulsion balls are very unstable and their interaction with the ocean wave spectrum is not known.

5. Conclusions

There are a number of conclusions that can be drawn from the experience of the 1986 Beaufort trials. The basic premise of these trials was that it is possible to determine dispersant effectiveness by use of remote sensing techniques alone. There is now substantial experimental evidence that there are a number of processes which interfere with the simple interpretation of the area of the slick as representing the amount of oil on the surface.

Since slick thickness cannot be readily measured from the air, it is attractive to consider the using of surface based equipment. Systems using sorbent pads have been developed by a number of workers (Belore, 1982). While the theory of such an apparatus is intrinsically simple, the results obtained from this equipment indicate very large errors. These errors arise from the sampling system itself, since the area of the water sampled is a function of the oil thickness, due to surface tension effects around the sampling head. There are problems with obtaining statistically significant samples at random locations in the slick. Determining the position in the slick at which the sample was taken is a problem since the slick is in continuous motion during the sampling program. Since it is not possible to location the sampling vessel within the slick to any degree of precision, it is not possible to obtain a representative selection of samples.

There are a number of novel approaches to the remote measurement of slick thickness conceived of by Reimer and Rossiter (1987) which may result in the ability to measure slick thickness from the air.

6. Acknowledgements

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SHIPBORNE RADAR AS AN OIL SPILL TRACKING TOOL

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Introduction

The capabilities of two x-band shipborne navigational radar units to detect oil slicks were evaluated during a joint Environment Canada-Minerals Management Service cruise offshore of Nova Scotia, Canada, in September 1987. Two series of spills were conducted; each consisted of five releases of five imperial barrels of Alberta Sweet Blend Mix (ASEM) crude and ASEM to which Bunker C had been added. The behavior of these slicks was monitored until the slicks had visually dissipated. Radar was used to track these slicks and the radar images were compared with visual observations when conditions permitted. Winds ranged from less than 10 to over 30 knots during the radar evaluation. Weather ranged from fog to rain to clear conditions.

The application of airborne x-band and synthetic aperture radar for slick detection is a proven technique with a number of worldwide operational units routinely available. Previous evaluation of shipborne radar (Axelsson, 1974) indicated that detection ranges for oil slicks were limited to approximately 1 kilometer even though the radar unit evaluated had a maximum range of 75 nautical miles. Discussions of factors influencing radar imagery conventionally describe a critical viewing angle of at least 20 degrees for sufficient reflection to yield a discernable pattern of sea surface conditions (Simanett, 1983). One evaluation of optimal antenna viewing angles (C-Core, 1981) indicated that 30 to 45 degrees from the vertical angle would be required. This lends credence to the findings of Axelsson and appears to explain the previously reported limited range of shipborne radar. However, evaluations during this cruise indicate that clear depictions of slicks are possible at ranges of 12 nautical miles or more.

One explanation of how the radar receives returns from the ocean surface is through back scattering. Microwave back scattering from the ocean surface may be due to Bragg scattering by the short (approximately 5 cm) waves for x-band radar causing a resonance in the microwave return to the antenna. This constructive interference is apparently necessary for discernable depiction of differences in sea surface texture except when breaking waves are present (Milgram, 1988). Bragg scattering is also a function of antenna viewing angle.

This evaluation of shipborne radar was predicated on the damping of short period waves by the slick and the ability of radar to detect and represent differences in the short period wave field.

Field Experiment

The joint Environment Canada-Minerals Management Service cruise to evaluate two oil spill chemical additives was conducted from the Canadian Coast Guard Cutter "Mary Hitchens" on September 9-10, 1987, offshore of Nova Scotia, Canada. Two shipboard radar units were used coincidentally to track and monitor each of the ten 5 imperial barrel oil spills during this exercise. It should be noted that an unidentified freighter transited the restricted exercise area and discharged an oil slick approximately 50 meters wide from horizon to horizon. The results of the evaluation of the chemical additives are reported elsewhere in these proceedings.

The two radars evaluated were the Sperry MK-340 and the Decca 914 with a Bright Track repeater. The Sperry MK-340 is an x-band radar with a horizontal beam width of 1.9 degrees and nominal ranges of 0.25, 0.5, 0.75, 1.5, 3, 6, 12, 14, 24, 48, and 120 nautical miles. The radar is a 50 kilowatt unit with its antenna approximately 50 feet above the ocean surface. The Decca 914 is also an x-band radar with nominal ranges of 0.25, 0.5, 0.75, 1.5, 3, 6, 12, 24, 48, and 60 nautical miles. The horizontal beam width is 1.9 degrees. The radar is a 25 kilowatt unit with an antenna height of approximately 40 feet above the ocean surface.

Results

Initial attempts to track the first five of the 5 barrel slicks over a range up to 12 nautical miles were unsuccessful with both units operating in standard navigational mode. Both radar units had sophisticated interference filters to reduce sea return and interference from rain. Approximately two hours were initially required to adjust the gain and sea and rain clutter filters to optimize the representation of the sea return. Once a relatively homogenous sea return was available on the radar, the observer analyzed areas of diminished sea return representing short wave damping due to the oil slick. The radar could subsequently be returned to navigational or slick detection mode by activating and deactivating the automatic filter program. The Decca did not offer the resolution of the Sperry and was less sophisticated so that initial adjustment for optimal sea surface return was more easily accomplished.

No photographic capabilities existed for the Sperry radar screen. The Decca Bright Track Unit allowed a wide range of screen brightness control and the following photographs were taken with this unit.

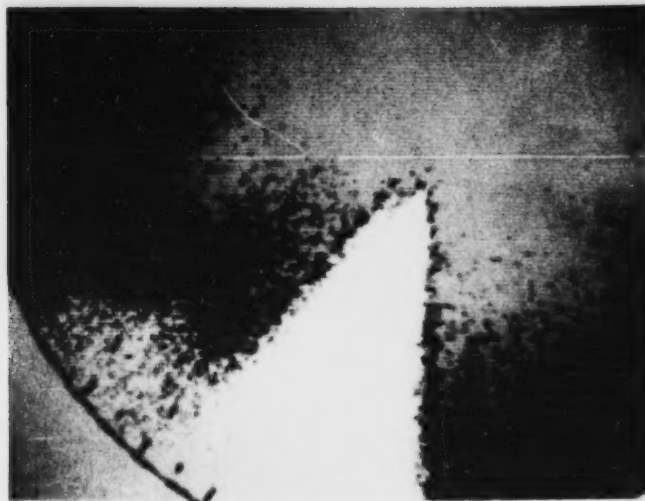


Figure 1 clearly shows the "mast shadow" artifact caused by the mounting of the radar unit just forward and starboard of the ship's mast. This pie-shaped hole in the sea return was apparent at all times.

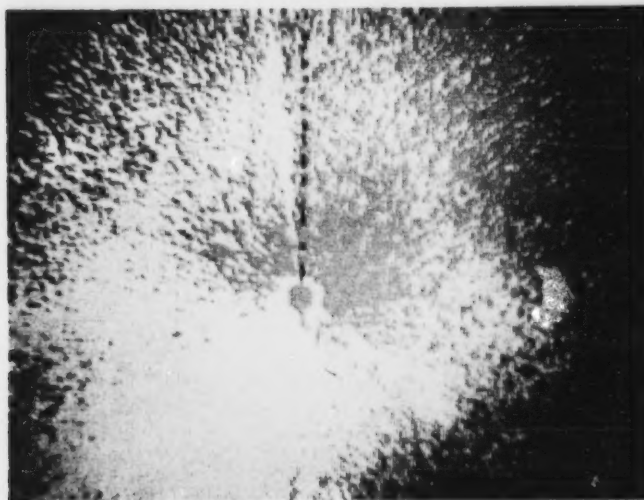


Figure 2. A five barrel slick (Slick No. 3) is visible at 11 o'clock (350 degrees relative). Range-3 nautical miles, winds 15-20 knots. The slick had deteriorated with patches of thick oil and mousse surrounded by sheen. The freighter's slick is visible at 9 o'clock (270 degrees relative).

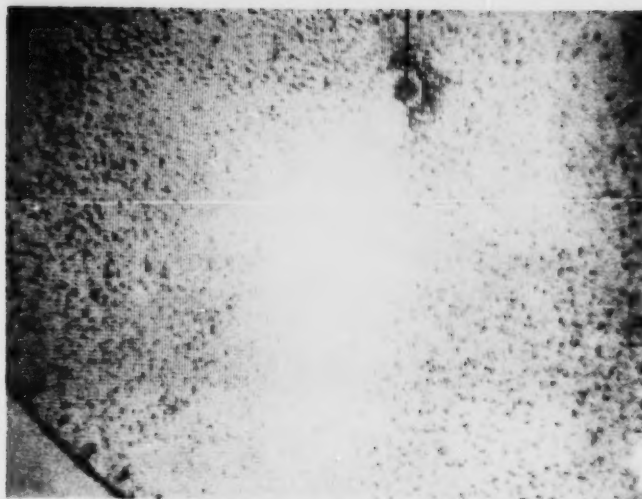


Figure 3. A slick is clearly visible from 6 to 7 o'clock (180-200 degrees relative) even though partially obscured by the mast shadow. Slick very light, mostly sheen, winds less than 10 knots. Range 3 miles.

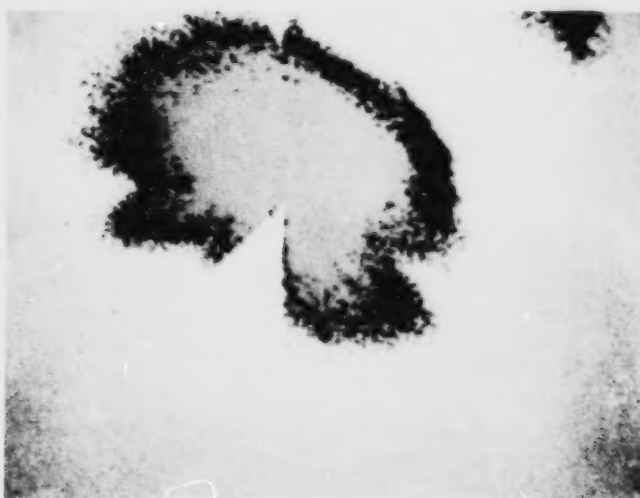


Figure 4 shows the mast artifact from 6 to 7 o'clock (180-200 degrees relative). The slick from the freighter is visible at 4 o'clock and 9 o'clock (110 and 270 degrees relative) and was a continuous slick. A heavily dissipated sheen is visible at 12 o'clock (360 degrees relative). Range is 12 nautical miles; winds 25-30 knots.

The Decca Unit did not have the resolution of the Sperry, therefore, the photographs do not offer the detail observed during the evaluations of the Sperry.

The presence of large swells coupled with breaking wind driven waves obscured the slicks when winds exceeded 30 knots. It is unclear whether relatively advanced and confused sea states or the rapid dissipation of the slick under these conditions, was responsible for the loss of detection. Perhaps both contributed to the apparent inability of either radar to find slicks in confused breaking seas. Fog and rain had no effect on the detection capabilities of either radar.

There was an apparent correlation between the observed thicker portion of the slicks and the radar image. As the slick dispersed into sheen thickness, the radar image became more indistinct. This technique apparently discerns thicker (more recoverable) slicks from less recoverable portions and could be used to guide recovery vessels, reducing unproductive efforts in slicks too thin for effective recovery.

Conclusions

Shipborne x-band radar can readily detect oil spills in a range of sea conditions if properly tuned.

Slicks were clearly detectable in winds up to 30 knots as long as major swells (8 to 10 feet) were not also present.

Slicks were detectable in 5-10 knot winds which were the minimum observed during the exercise.

Requirements for tuning the radar to optimize sea return vary with the sophistication of the unit. The higher the sophistication the more difficult the initial tuning.

Radar is a readily available tool to most responders and its use can expand slick tracking and can eliminate many of the detection problems associated with fog, rain, darkness, and relatively high sea states.

Further evaluation with a range of oils and sea states is required to quantify the limits of this technique.

Acknowledgements

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Disclaimer

The mention of specific products in this report does not constitute or imply an endorsement by the MMS or the author.

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LABORATORY AND MESOSCALE TESTING
OF ELASTOL[™] AND BRAND M DEMOUSSIFIER*

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ABSTRACT

Recently, 2 promising oil spill treating agents have been developed. They are: Elastol, a viscoelastic enhancing agent, and Brand M Demulsifier/Demoussifier. Preliminary testing of the products were encouraging and as a result, the U.S. Minerals Management Service and Environment Canada decided to conduct further testing on a larger scale. These planned tests included wave basin testing and an offshore ocean trial.

Results from laboratory and tank testing of Elastol were presented at the 1987 AMOP Conference. Complete results from that study are presented in Bobra et.al.(1987a). This paper starts off with a brief summary of those findings and then presents a summary of the work performed to develop applicators suitable for mesoscale use for the 2 treating agents and to test the effectiveness of the products when thus applied.

SUMMARY OF PREVIOUS FINDINGS

The bulk of the work presented at the 1987 AMOP Conference was performed within the laboratory and on a small scale. The first phase of that work examined what effect Elastol had on specific oil properties and its effect upon the physical processes which occur to spilled oil. A simple and portable "die swell" apparatus was constructed in order to obtain a quantified characterization of the elastic component of treated oils. Die swell is a physical phenomenon associated with elastic fluids and manifests itself when the fluid is forced through a small opening (or die); the diameter of the extrudate swells to a diameter greater than the die opening. By measuring the degree of die swell exhibited, a relative indication of elasticity could be obtained.

[™] Elastol is a registered trademark of General Technology Applications Inc.

* Brand M is a surfactant based demulsifier formulated by Environment Canada.

A series of bench-scale experiments were performed to determine the viscosity and elasticity of Elastol-treated oils at different concentrations, temperatures and mixing times. Elastol was applied to a 7.4 mm thick layer of oil contained in a covered crystallizing dish and then the oil was either subjected to no mixing or to mixing at 80 RPM on a gyratory shaker table. Eight crude oils and a diesel fuel were tested. Each exhibited viscoelastic behaviour when treated with 600 to 6000 ppm of Elastol. All oils exhibited some degree of elasticity within 15 minutes of Elastol application. The time for Elastol to dissolve and take effect, and the degree of elasticity was different for each oil. Generally, the more viscous oils attained a higher degree of elasticity but took longer to react than the less viscous oils. It was found that both mixing and higher temperatures improved the rate of dissolution and the degree of elasticity attained.

The application of Elastol to oil had no effect upon the flash point and caused only a very minor reduction in the rate of evaporation.

Experiments were performed in which Elastol was applied to oil contained within a boomed area upon a water surface. Time and Elastol concentration were varied. The final spill area covered by the slick after being released from the boom was compared to the area of an untreated control slick. The effectiveness of Elastol to reduce slick spreading increases with time. It was also found that the time for Elastol to dissolve and take effect was much shorter for a less viscous oil.

The emulsification behaviour of Elastol-treated oils was examined in an apparatus that rotated mixtures of seawater and oil contained in 500 mL Fleakers according to the rotate/rest cycle of Mackay and Zagorski (1982). Elastol was added to the oil one hour prior to starting the rotating. Ten oils of varying emulsion behaviour were tested at 0°C and 15°C. For two of the oils (Amaligak and Tarsiut), the addition of Elastol increased their tendencies to form water-in-oil emulsions. For the other eight oils, the addition of Elastol had either no effect or caused a decrease in the emulsification tendency. In general, the emulsions formed by Elastol-treated oils were observed to have a lower water content than untreated oils. In addition, a limited number of runs were performed where Elastol was added to oil that was already emulsified. These tests indicated that Elastol could still reduce the degree of emulsification.

During the second phase of the study, experiments were performed in a 35 litre tank equipped with an oscillating hoop wave generator. Alberta Sweet Mixed Blend (ASMB) crude and a 50/50 mixture of ASMB and Bunker C were treated with Elastol concentrations of up to 6000 ppm, and tested at two mixing energies, two temperatures, and two water salinities. Each test was 3 hours in duration and both water and oil samples were taken during the run. Water samples were analysed for oil content and oil samples were analysed for water content, viscosity, elasticity as indicated by die swell measurements, and weathering due to evaporation (determined by GC).

In general, the application of Elastol to oil reduced the extent of emulsification experienced by the slick and as a consequence of this, the treated slicks had lower viscosities than untreated slicks which tended to be heavily emulsified. Therefore, the increase in viscosity due to the elasticity imparted by Elastol was small compared to the increase due to emulsification. However, under conditions which are highly favourable for emulsification, the ability of Elastol to limit the extent of emulsification was slight and the subsequent increase in viscosity was not prevented.

All oils tested under the varying conditions exhibited elastic behaviour within 15 minutes of Elastol application. As expected, increasing the concentration of Elastol resulted in a higher degree of elasticity. At 15°C the oils treated with 6000 ppm of Elastol exhibited a high degree of viscoelasticity after 1 to 2 hours. At 0°C, the time required for Elastol to dissolve was longer. It was also found that an oil, like the 50/50 mixture, which has a strong tendency to emulsify, will exhibit less elasticity than an oil which has less of a tendency to emulsify when treated with the same concentration. Therefore, it would appear that in certain circumstances, Elastol can suppress emulsification but that in other circumstances where the oil has a strong tendency to emulsify, the emulsification process may inhibit the development of elasticity.

The results from the small-scale wave generating tank experiments showed that the application of Elastol did not significantly affect the rate of oil evaporation.

The effectiveness of two surfactant-based treating agents were tested on Elastol-treated oil. Tests with Corexit 9527 dispersant in the wave generating tank showed that an Elastol-treated slick was significantly more resistant to chemical induced dispersion. On the other hand, tests in the emulsion formation apparatus showed that Elastol had no effect on the performance of Brand S emulsion inhibitor.

Two days of wave basin tests were performed at the Esso Research Facility in Calgary, Alberta. For each test, 75 litres of Norman Wells crude was placed in a boom and then manually dosed with 6700 ppm of Elastol. The tests ran for 4 hours and wave heights of 25 and 50 centimeters were used. Observations of the slicks indicated that at the wave energies applied, there was no sign of degradation in elasticity and that in fact the slicks became progressively more elastic with time. At the higher wave energy, the time required for Elastol to dissolve was less and the degree of elasticity achieved was greater. Oil recovery from the boomed area was done with a Morris MI-2C skimmer. About 93% of the original volume spilled was recovered and the recovered oil appeared to contain no free water.

The report on the work performed on mesoscale application is comprised of two parts. The first part describes the development and laboratory testing of applicators for the oil spill products. The second part deals with mesoscale wave tank testing using these applicators. Complete results are presented in Bobra et.al.(1987b).

Part 1 - DEVELOPMENT AND TESTING OF MESOSCALE APPLICATORS

INTRODUCTION

This study was undertaken to develop and test methods of applying Elastol and Brand M for mesoscale applications. In particular, the objectives of the study were:

- i. to develop applicators for dispensing Elastol and Brand M;
- ii. to test and adjust these applicators to deliver the desired dose rates with a relatively uniform distribution pattern;
- iii. to measure the effectiveness of Elastol and Brand M when applied by these systems.

APPLICATOR SYSTEMS

An extensive review of potential application systems was conducted. The candidate systems were critically evaluated in terms of the following criteria:

- i. distribution characteristics - the applicator should dispense the treating agent over a relatively large area with a uniform distribution pattern and deliver a flowrate that will dispense the treating agent in an acceptable period of time for the range of Elastol and Brand M doses proposed for the mesoscale trials (500 to 9000 ppm for Elastol and 250 to 4000 ppm for Brand M);
- ii. portability and ruggedness - necessary for field use;
- iii. safety - the equipment must be safe to use in the presence of flammable materials;
- iv. simple to operate.

After careful evaluation, a Campbell-Hausfeld Power Blast Model AT1210 (more commonly known as a sandblaster) was chosen to dispense both spill treating agents. A schematic diagram of the system is illustrated in Figure 1. The system has a 5 gallon (19L) capacity and uses compressed air to dispense its charge. A vented hopper was added to the blaster for the application of Elastol. This was necessary to ensure a continuous flow of Elastol and to ensure that all Elastol placed into the system is dispensed. No system modification was required for Brand M application.

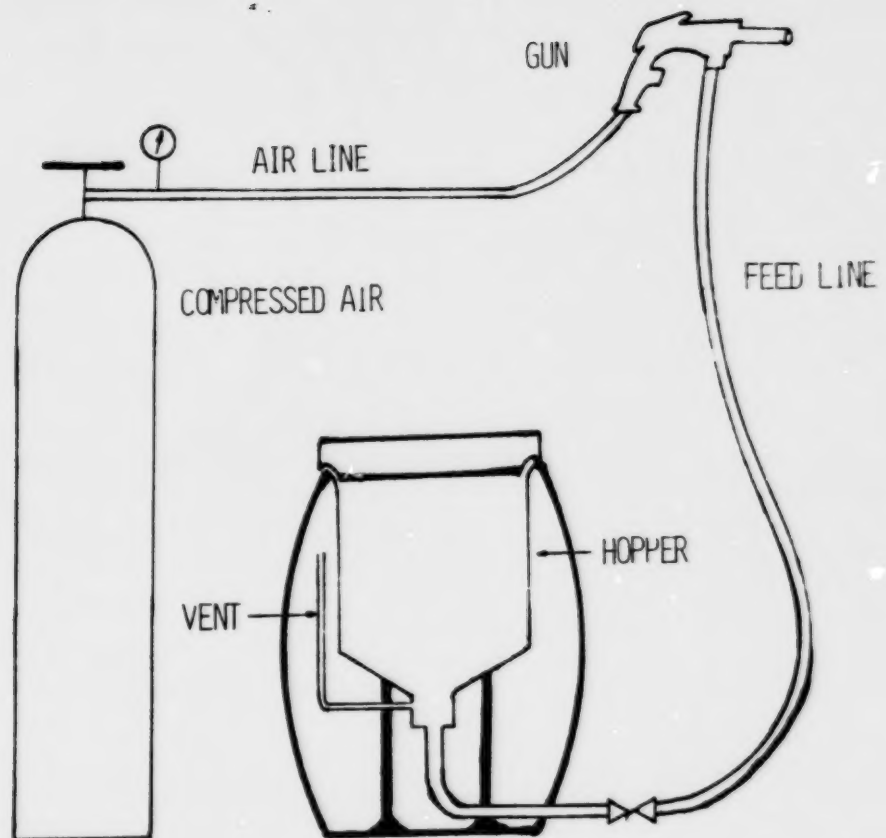


FIGURE 1 . SCHEMATIC DIAGRAM OF APPLICATOR.

During this work, the supply of compressed air came from the lightweight cylinders used for the Scott backpack breathing apparatus. These cylinders have a capacity of 45 ft³ (1.3 m³) at 2216 psi (15,280 kPa). The air pressure regulator was set at 40 psi (276 kPa) for the application of Elastol and at 20 psi (138 kPa) for the application of Brand M. These settings were determined to give the optimum spray patterns and dose rates. One air cylinder provided 7.5 minutes of air for the Elastol applicator and 12 minutes for the Brand M applicator. Two or more cylinders can be used in a cascade configuration for longer application times.

The demulsifier was discharged as a 50% solution of Brand M in a commercial solvent Isopar M. This particular solvent was chosen because of its low volatility and toxicity. The reasons for mixing the demulsifier with solvent were:

- i. to reduce its viscosity in order to improve flow characteristics (pure Brand M has a viscosity of 1200 cP at room temperature);
- ii. to promote better diffusion and mixing of the demulsifier's active ingredients with the spilled oil;
- iii. to increase the volume of the treating agent to be applied and thus the dispensing time, thereby allowing a more thorough and even application of Brand M to the oil slick, especially at the lower demulsifier-to-oil concentrations.

DISTRIBUTION EXPERIMENTS

Procedure

The flowrates and distribution patterns of Elastol and the Brand M solution were determined by conducting a set of indoor experiments in which the spill treating agents were dispensed from a stationary position onto a grid marked floor. For each applicator, two tests were performed: one with the spray gun positioned parallel to the ground and the other with the gun positioned 45 degrees downward. In both tests, the gun was fixed at a height of one metre above the ground. A preweighed dose of treating agent was dispensed onto the grid marked floor, and at the end of the experiment, the amount of treating agent in each square was determined. The total dispensing time was also recorded and the average flowrate calculated. Several tests were conducted outdoors to examine how the applicators would perform when subjected to the influence of wind.

Results

The distribution patterns for the sprayed Elastol and Brand M solution are presented in Figures 2 to 5. From the Figures, it can be seen that over 90% of the dispensed Elastol settled in an area 2 m wide by 4 m long. The area in which most of the Brand M settled was smaller; approximately 92% of the demulsifier solution was collected in an area 1 m wide by 3 m long. The total area covered was greater for Elastol when the gun was pointed horizontal to the ground (26 m^2), as opposed to 45 degrees downward (20 m^2). The mass flux was calculated to be $0.14 \text{ g/m}^2\text{s}$ and $0.18 \text{ g/m}^2\text{s}$, respectively. On the other hand, the direction of the gun did not affect the total area coverage (and flux) for the demulsifier. The respective values were determined to be 5.5 m^2 and $0.29 \text{ mL/m}^2\text{s}$.

The calculated flowrates were 3.6 g/s for Elastol and 1.6 mL/s for the demulsifier solution. The air pressure was set such that the lowest possible flowrates were obtained without compromising the smooth discharge of the treating agents. This was thought to give more flexibility to the operators at the field trial and would allow them to cover the oil slick more evenly, especially at low treatment levels.

The performance of the applicators under calm outdoor conditions (wind speeds of up to 8 km/hr) was observed to be similar to that of the indoor tests. At higher wind speeds, the influence of the wind could be compensated for, in part, by directing the spray more towards the ground.

LABORATORY TANK TESTS

Procedure

Laboratory testing was conducted in an 89 cm diameter tank equipped with an adjustable speed oscillating hoop (85 cm in diameter) wave generator. The tank was filled with 336 L of 33 ppt salt water (water temperature: $15 \pm 2^\circ\text{C}$) and the wave generator was set at a speed of 46 RPM.

For the demulsifier tests, the Brand M solution was sprayed onto a 1 mm thick slick of "Emulsifying Mix oil" (50-50 mixture of Alberta Sweet Mixed Blend crude and Bunker C fuel oil) from a height of 1 m above the slick surface. Three separate experiments were performed in which the emulsion breaker was applied at Brand M-to-oil ratios of 1:500, 1:2000 and 1:4000. Oil samples were taken periodically over a 24 hour period to determine the water content of the oil slick and hence the effectiveness of Brand M in inhibiting emulsification.

An additional experiment was performed in which a 1:500 dose of the demulsifier was sprayed onto the oil slick after allowing it to emulsify for 3 hours. A second 1:500 dose was applied at the 4.5 hour mark. The water content was monitored at regular intervals.

FIGURE 4 . Distribution Pattern of Sprayed Brand 'M' Solution

Conditions: -Flowrate: 1.6 ± 0.2 ml/s

-Solution: 50% Brand 'M' / 50% Isopar 'M'

-Sprayed Parallel to the Ground

		3.8 ± 1.0 (0.246 $\pm$ 0.065)	3.8 ± 1.0 (0.246 $\pm$ 0.065)	Beyond 3m
		2.7 ± 0.6 (0.175 $\pm$ 0.039)	2.7 ± 0.6 (0.175 $\pm$ 0.039)	3m
		6.6 ± 0.9 (0.428 $\pm$ 0.058)	6.6 ± 0.9 (0.428 $\pm$ 0.058)	2.5m
0.1 (0.0016)	11.3 ± 1.0 (0.732 $\pm$ 0.065)	11.3 ± 1.0 (0.732 $\pm$ 0.065)	0.1 (0.0016)	2m
0.1 (0.0016)	11.9 ± 0.9 (0.771 $\pm$ 0.058)	11.9 ± 0.9 (0.771 $\pm$ 0.058)	0.1 (0.0016)	1.5m
	10.3 ± 0.3 (0.667 $\pm$ 0.019)	10.3 ± 0.3 (0.667 $\pm$ 0.019)		1m
	3.2 ± 0.9 (0.207 $\pm$ 0.058)	3.2 ± 0.9 (0.207 $\pm$ 0.058)		0.5m

Values are in weight percent. Values in brackets are in $\text{ml/m}^2\text{s}$

FIGURE 5. Distribution Pattern of Sprayed Brand 'M' Solution

Conditions: -Flowrate: 1.6 (0.2 ml/s

-Solution: 50% Brand 'M' / 50% Isopar 'M'

-Sprayed 45° Downwards

[illegible]

Values are in weight percent.
Values in Brackets are in ml/m²s.

For the Elastol tests, the Elastol applicator was used to dispense the treating agent at doses of 1500 and 3000 ppm onto a 1 mm thick slick of fresh Alberta Sweet Mixed Blend crude oil. Oil samples were taken hourly to determine the elasticity using the die swell procedure as outlined in Bobra et.al. (1987a). The Elastol used was the latest version formulated by GTA, "80/20 Elastol", and had a different composition than the Elastol used in the previous laboratory study.

Results

i. Brand M

The results of the demulsifier application tests in the large oscillating hoop tank are presented as a plot of water content of surface oil versus time in Figure 6. It is clear that in the control slick to which no demulsifier was applied, the oil emulsified to a stable water content of 80% within the first hour. The other curves show that the addition of the demulsifier in the dose range from 1:4000 to 1:500 reduces the degree of emulsification and the rate of water uptake. Approximately 6 hours were required for treated slicks to attain a constant water content.

It is peculiar to note that considering the large difference in treatment doses, there was little difference in the water content values of the three treated slicks. These results are similar to those found in the wind/wave tank tests of Brand S emulsion inhibitor (S.L. Ross, 1987). In an attempt to further examine this behaviour, oil/seawater interfacial tension was measured as a function of Brand M concentration. These measurements are plotted in Figure 7. Pure oil and seawater has an interfacial tension of 26 dynes/cm. Figure 7 shows that the addition of Brand M (at Brand M-to-oil ratios of 1:10,000 to 1:500) significantly reduces the interfacial tension, but that there is only a slight drop in the interfacial tension from about 15 to 14 dynes/cm with a 20 factor increase in Brand M concentration. This may, in part, account for the results obtained in Figure 6. Nevertheless, these results seem to indicate that only a small dose of demulsifier may be required to effectively prevent extensive emulsion formation.

Figure 8 shows the results of the test in which the demulsifier was applied to emulsified oil. A 10% drop in the water content was observed after the first application and a further 15% decrease was obtained following the second addition. This indicates that the demulsifier is also effective in reducing the water content of oil that is already emulsified.

The test results show that the applicator was successful in effectively delivering the demulsifier to oil spilled on water.

FIGURE 6 . Water Content of Slick as a Function of Time

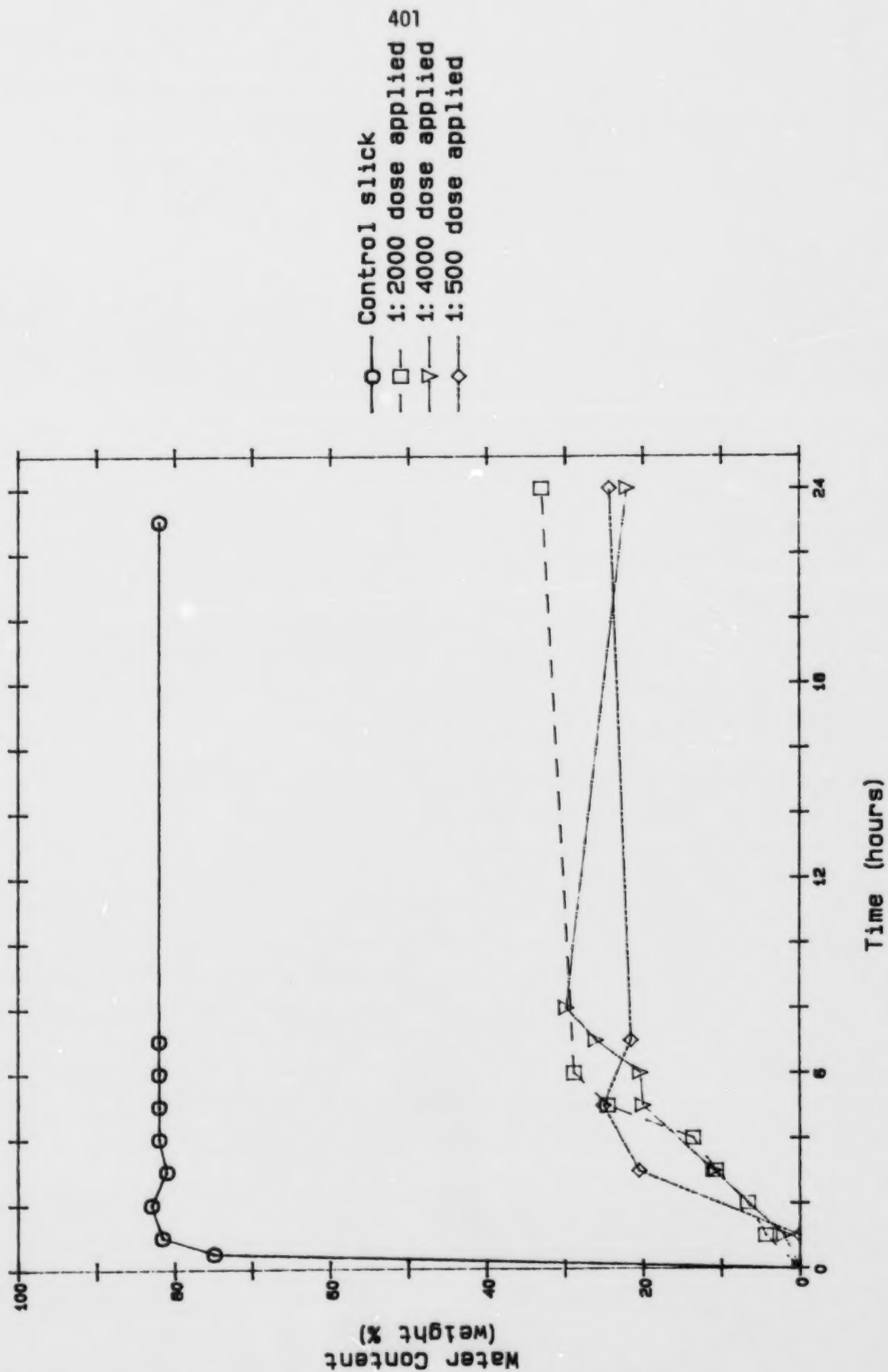


FIGURE 7 . Interfacial Tension of Oil/Seawater
as a Function of Brand M Dose

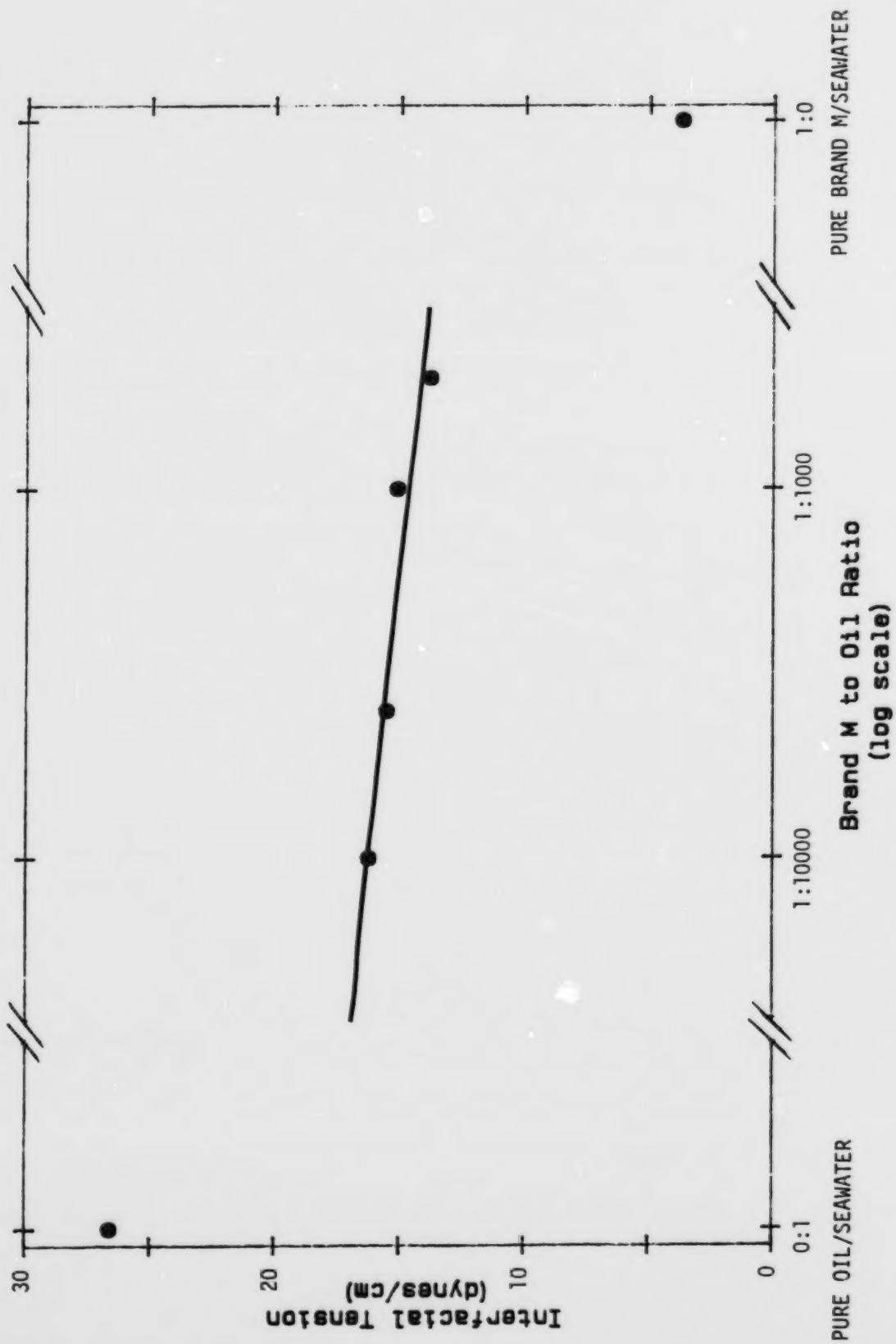
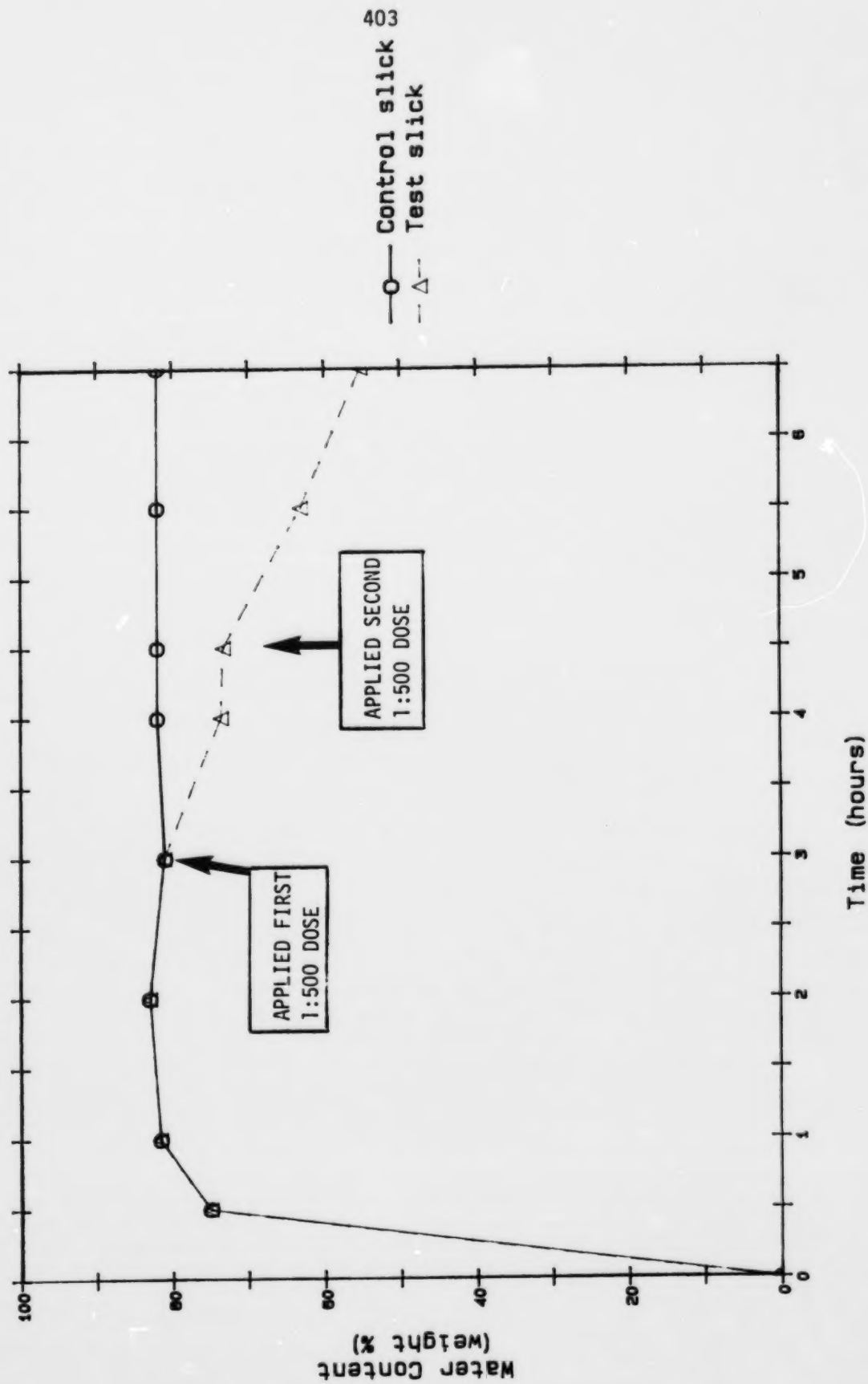


FIGURE 8 . Water Content of Slick as a Function of Time
When Treated with Brand "M" Demulsifier



ii. Elastol

The results of the Elastol application tests are presented in Figure 9 which plots the die swell ratios as a function of time. The results show that Elastol applied in this manner was effective in imparting elastic behaviour to the oil slicks within one-half hour after application as indicated by the greater-than-one die swell ratios, and that increasing the Elastol concentration resulted in greater elasticity. Furthermore, observation of the slicks showed a fairly even elasticity development throughout the oil, indicating a relatively even distribution of the treating agent during the application procedure.

PART 2 - REPORT ON MESOSCALE OF ELASTOL AND BRAND M

INTRODUCTION

Four days of testing were conducted by M. Pingas in the outdoor test basin at the Esso Research Facility in Calgary. The previously described applicators were used for applying the treating agents. The purpose of the testing was:

- i. to examine the performance of the applicators under conditions that loosely resemble those found at environmental spill situations;
- ii. to determine the effectiveness of the agents when applied in this manner and under these conditions;
- iii. to compare the behaviour of treated slicks to slicks left untreated.

EXPERIMENTAL

A schematic diagram of the basin is shown in Figure 10. The dimensions of the basin are 15 m x 19 m with a maximum depth of 2 m. For these tests, the basin was filled with fresh water. Two circular boom configurations of 5m in diameter were positioned side by side and parallel to the wave generating flap. With the booms placed in such a configuration, slicks can be placed in each of the boomed areas and then subjected to identical wave conditions. For each day of testing, one slick was treated with an agent and the other slick was left untreated to serve as a control.

After applying the treating agent, the wave generators were turned on to produce waves 10 cm in height. The wave generators were turned off during sample taking and during oil recovery with the skimmer. Samples were taken from both slicks at approximately logarithmic intervals and dynamic viscosities were measured using a Fann viscometer.

FIGURE 9 . Die Swell Ratio versus Time

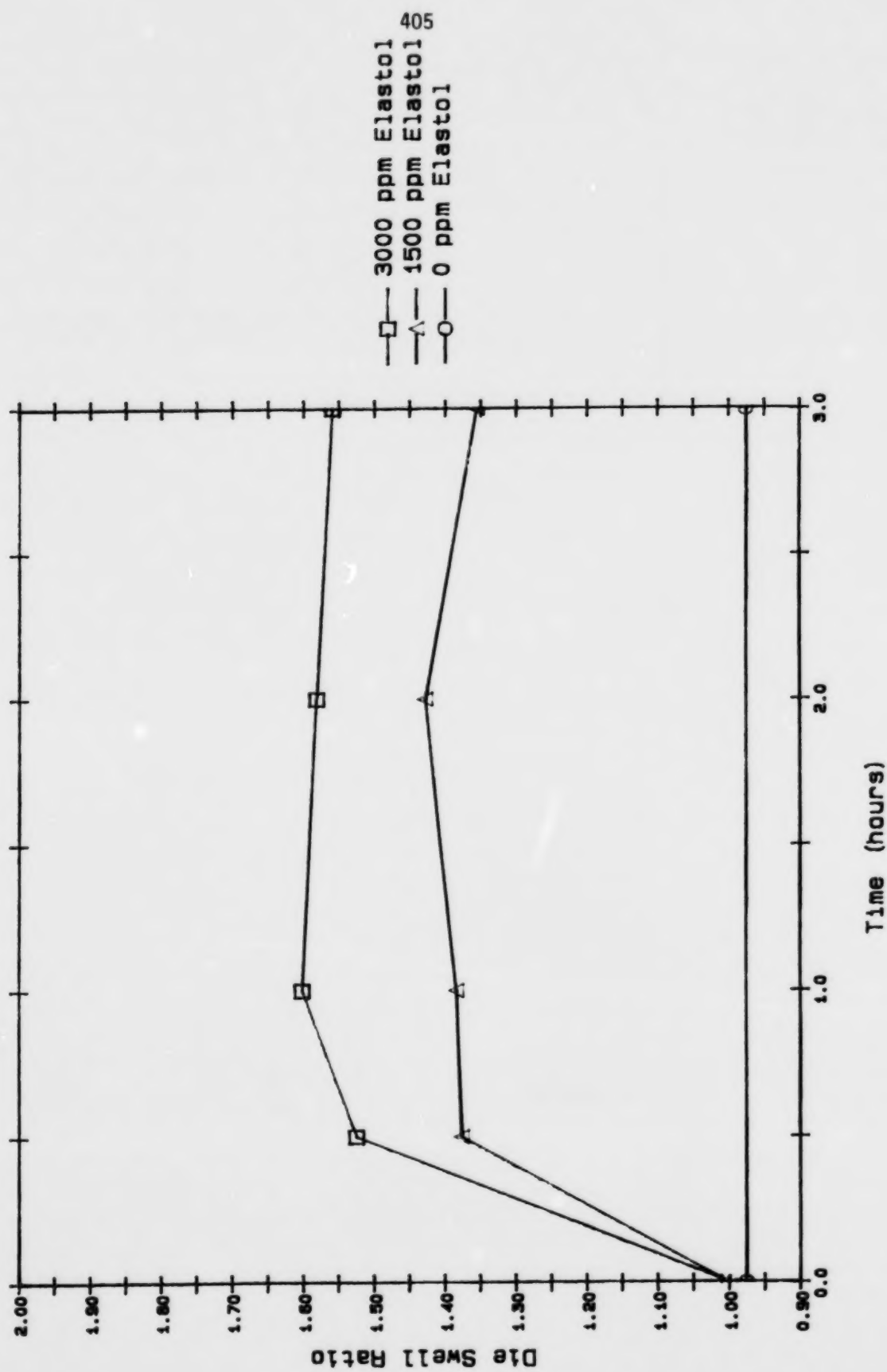
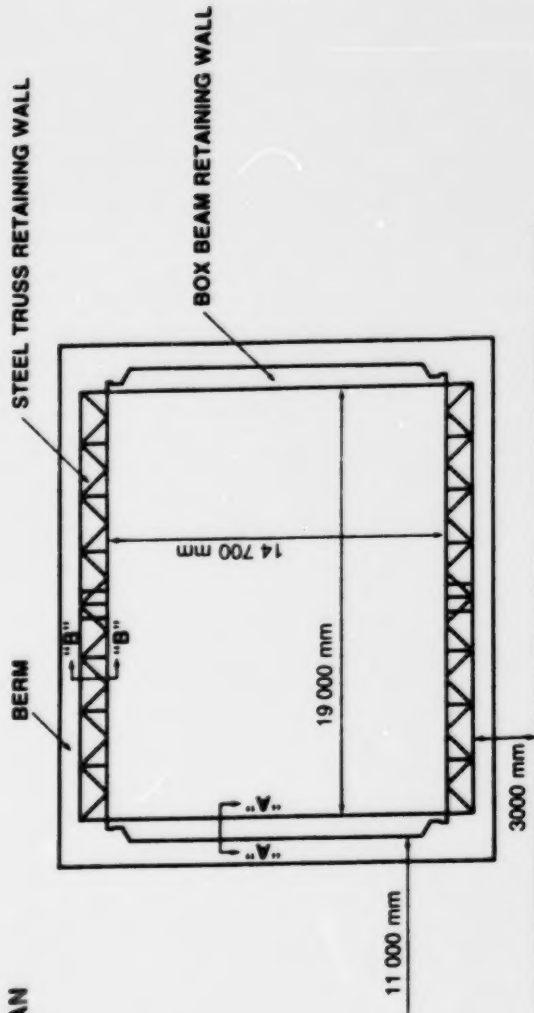


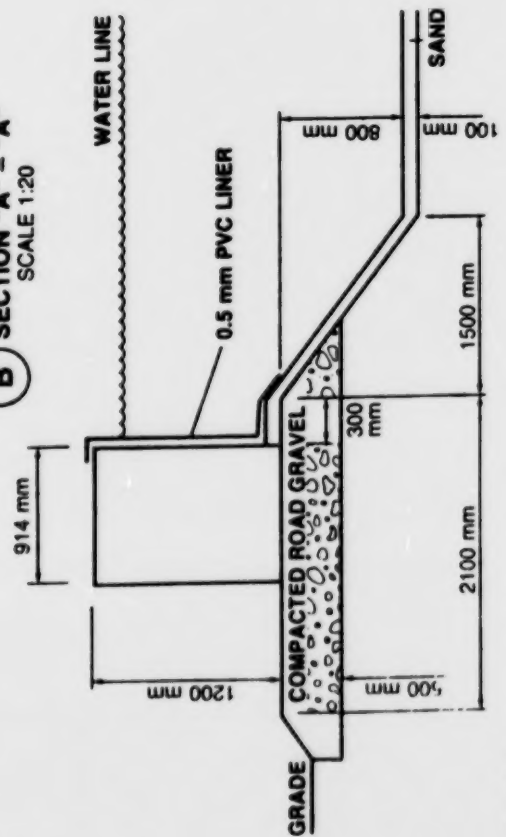
Figure 10

Schematic Plans of Test Basin

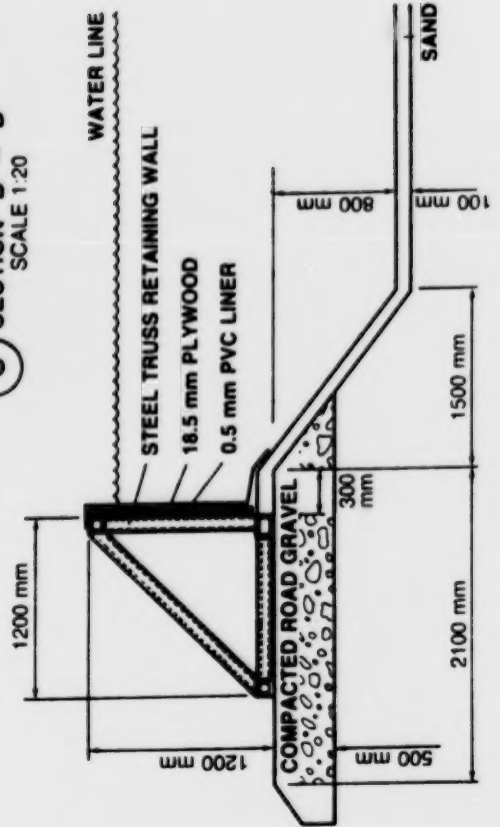
A OVERHEAD PLAN
SCALE 1:100



B SECTION "A" - "A"
SCALE 1:20



C SECTION "B" - "B"
SCALE 1:20



At the end of each test day, the oil contained in the booms was recovered by a Morris MI-2C skimmer. The recovered oil was allowed to settle overnight in order to separate the oil and water. Recovery rates were calculated from the volume of oil recovered and the skimmer's operating time.

RESULTS

Day 1 - Application of 2000 ppm Brand M Demoussifier

The test oil used was a half-half mixture of Federated crude oil and tar. This mixture was used because preliminary tests showed it had a strong tendency to form stable emulsions. Some diesel fuel was inadvertently added to the test oil thus producing a mixture slightly different than that used on Day 2.

The measured viscosities are given in Table 1 and Figure 11. The higher viscosity values recorded for the control slick indicate that the untreated oil was forming an emulsion more readily than the treated oil. This was also supported by the physical appearance of the slicks. The control slick had reddish-brown streaks in it, indicating formation of "chocolate mousse". On the other hand, the treated slick remained black in colour and the slick surface was distinctly smooth and glossy.

The slicks also showed a marked difference in their recoverability by the skimmer. The untreated oil was recovered at more than twice the rate of the treated oil. It is suspected that this is due to the lower interfacial tension of the treated oil caused by the demoussifier.

Day 2 - Application of 2000 ppm Brand M Demoussifier

The test oil was a half-half mixture of Federated crude oil and tar. The viscosity results are presented in Table 2 and Figure 11, and as in Day 1, the viscosity of the control slick was higher than the treated slick. The difference in oil recoverability was less dramatic than in Day 1, but the untreated oil had a recovery rate of about 37% higher than the treated oil.

During the course of the day, another quick test of opportunity was performed. A small mat of oil which had escaped from the boom of the control slick on the previous day was floating at one end of the tank. This oil was highly emulsified and had the typical "chocolate mousse" appearance. A small amount of demoussifier was poured directly onto the oil mat and observations were taken. Over a period of minutes, the oil's colour turned to black and then the oil broke up into a thinner, shiny slick.

TABLE 1: NUMERICAL RESULTS FROM THE ESSO TANK TESTS

Day 1: 2000 PPM DEMOUSSIFIER TRIAL

Oil: 70L half Federated crude oil and half tar (approx.)
(contaminated with small amount of diesel fuel)

Viscosity (cP or mPa.s)			
Time (min)	0	40	85
test slick	64(± 2)	113(± 7)	190(± 42)
control	64(± 2)	169(± 1)	324(± 25)

Recovery by Skimmer

	Volume (L)	Rate (L/min.)
test slick	46	0.93
control	32	2.1

Overall Conditions:

Wave Height: 10 cm
Water temperature: 19 deg C
Air temperature: 20 to 28 deg C, depending on time of day
Wind speed: 0 to 5 km/hr, direction and speed variable

TABLE 2: NUMERICAL RESULTS FROM THE ESSO TANK TESTS

Day 2: 2000 PPM DEMOUSSIFIER TRIAL

Oil: 70L half Federated crude oil and half tar

Viscosity (cP or mPa.s)				
Time (min)	0	20	90	210
test slick	176(± 3)	176(± 5)	203(± 8)	350(± 160)
control	176(± 3)		383(± 23)	668(± 82)

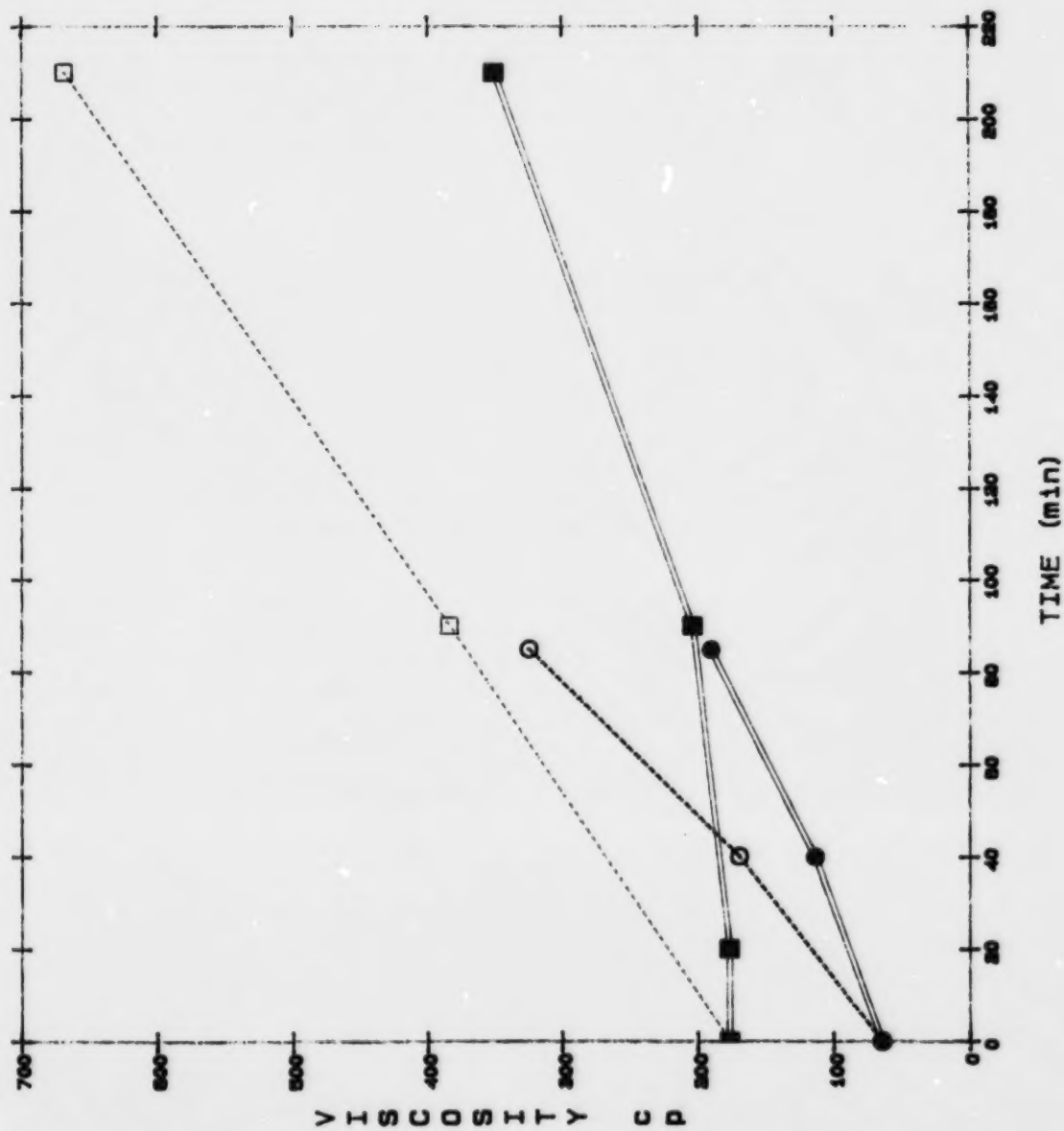
Recovery by Skimmer

	Volume (L)	Rate (L/min.)
test slick	57	0.95
control	60	1.3

Overall Conditions:

Wave Height: 10 cm
Water temperature: 19 deg C
Air temperature: 20 to 28 deg C, depending on time of day
Wind speed: 0 to 5 km/hr, direction and speed variable

Figure 11. RESULTS OF THE DEMOUSSIFIER TANK TESTS



Day 3 - Application of 4000 ppm Elastol

The test oil used was Federated crude oil. The numerical viscosity results, given in Table 3 and Figure 12, show the dramatic increase in viscosity caused by the addition of Elastol.

At the end of the day, it was decided that a quick burning experiment be conducted prior to recovering the oil. With the wave generator turned off, the treated slick (viscosity of 4825 cP) was released from the boom. A simple ignition device consisting of cubes of solidified barbecue lighter fuel on a piece of styrofoam was lit and then placed in the thickest portion of the slick. The flame did not propagate but oil in the immediate vicinity of the device burned with the characteristic popping sound of a burning slick. The flame was sustained for 35 minutes. Examination of the device showed that most of its components remained intact indicating that oil had sustained the burn. The oil slick was thin and by visual estimation was not of sufficient thickness to permit flame propagation. The oil remaining after the burn experiment was recovered by the skimmer. The recovery rate was not recorded but it was observed that the skimmer was collecting oil at maximum capacity.

Day 4 - Application of 2000 ppm Elastol

The test oil was Norman Wells crude oil. Figure 12 and Table 4 show that the Elastol treated slick had a higher viscosity than the control.

During the course of the test, the control slick was observed to be taking up water and the characteristic reddish-brown appearance of mousse was spreading throughout the slick. At 140 minutes, a 500 ppm dose of Brand M was added to the control slick to prevent further emulsification. The demoussifier was poured directly onto the slick and in a non-uniform manner. Despite this, the entire slick surface gradually turned black and took on the distinctive glossy shine. The same 500 ppm demoussifier treatment was applied to the Elastol-treated oil to ensure no experimental bias.

The recovery rates are shown in Table 4; the Elastol treated oil was recovered at more than twice the rate of the untreated oil. Indeed, the treated oil resulted in flooding of the skimmer indicating that the skimmer was operating at capacity. Therefore, the recoverability of the oil may be more than that indicated by the capacity of the Morris MI-2c skimmer. This also shows that the decrease in recoverability caused by the demoussifier can be remedied by the addition of Elastol, and it confirms previous laboratory tests that show Elastol and Brand M can be employed together.

TABLE 3: NUMERICAL RESULTS FROM THE ESSO TANK TESTS

Day 3: 4000 PPM ELASTOL TRIAL

Oil: 75L of Federated crude

time (min)	Viscosity (cP or mPa.s)			
	0	25	110	270
test slick	5($\pm$ 0.5)	22($\pm$ 3)	128($\pm$ 18)	4825($\pm$ 75)
control	5($\pm$ 0.5)	12($\pm$ 0.5)	28($\pm$ 5)	229($\pm$ 25)

Recovery by Skimmer

	Volume (L)	Rate (L/min.)
test slick	burn attempt -- did not propagate	
control	100 (much H ₂ O)	2.9

Overall Conditions:

Wave Height: 10 cm
 Water temperature: 19 deg C
 Air temperature: 20 to 28 deg C, depending on time of day
 Wind speed: 0 to 5 km/hr, direction and speed variable

TABLE 4: NUMERICAL RESULTS FROM THE ESSO TANK TESTS

Day 4: 2000 PPM ELASTOL TRIAL

Oil: 75L Norman Wells Crude

time (min)	Viscosity (cP or mPa.s)			
	0	40	120	270
test slick	6.7($\pm$ 0.2)	41($\pm$ 5)	173($\pm$ 28)	356($\pm$ 21)
control	6.7($\pm$ 0.2)	19($\pm$ 1)	75($\pm$ 28)	136($\pm$ 14)

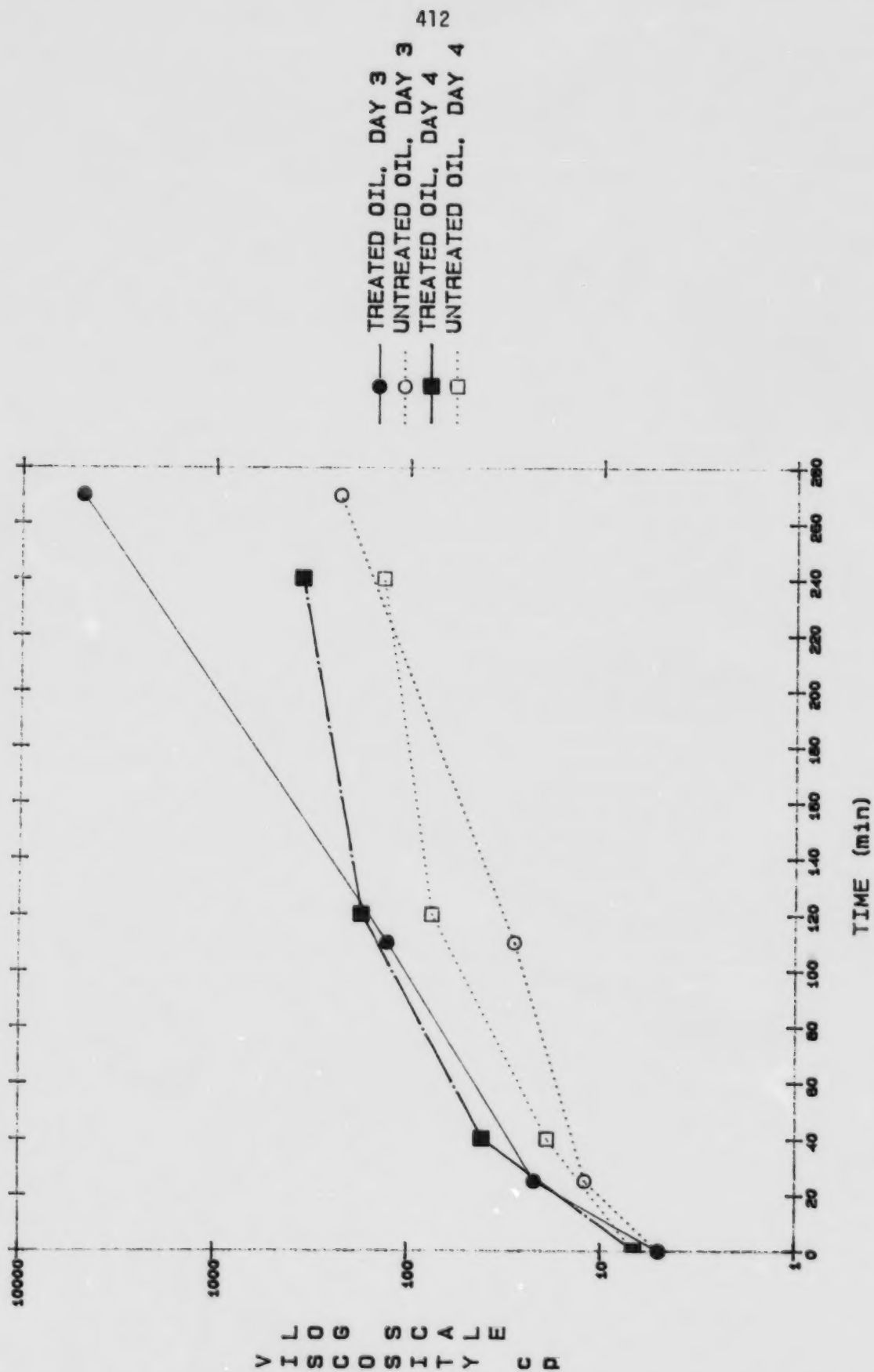
Recovery by Skimmer

	Volume (L)	Rate (L/min.)
test slick	90	5.0
control	46	2.3

Overall Conditions:

Wave Height: 10 cm
 Water temperature: 19 deg C
 Air temperature: 20 to 28 deg C, depending on time of day
 Wind speed: 0 to 5 km/hr, direction and speed variable

Figure 12. RESULTS OF THE ELASTOL TANK TESTS



CONCLUSIONS

Mesoscale application systems have been developed for the two new oil spill treating agents, Elastol and Brand M. The main components of both applicators are a commercially available sandblaster and portable air cylinders. Tests conducted during this study showed that from a fixed position, the Elastol applicator could distribute the treating agent up to a distance of 7 m and cover an area of 26 m². Similarly, the Brand M applicator could spray up to 4 m and cover an area of 5.5 m². A solvent, Isopar M, was chosen as a carrier/solvent for Brand M application in order to improve its spray characteristics and to promote better mixing with oil.

Tests were conducted in a large laboratory wave-generating tank to measure the effectiveness of the treating agents when applied from these systems. The results obtained from these tests were similar to those of previous laboratory studies; they showed that Brand M demoussifier can effectively reduce the degree to which oil emulsifies and that Elastol renders oil viscoelastic.

The applicators proved to work well during the four days of wave basin testing. Slicks treated with Brand M had lower water content than untreated control slicks subjected to the same conditions. As Figure 13 shows oil recoverability (as determined by a skimmer) was decreased by the demoussifier treatment but this could be remedied by adding Elastol.

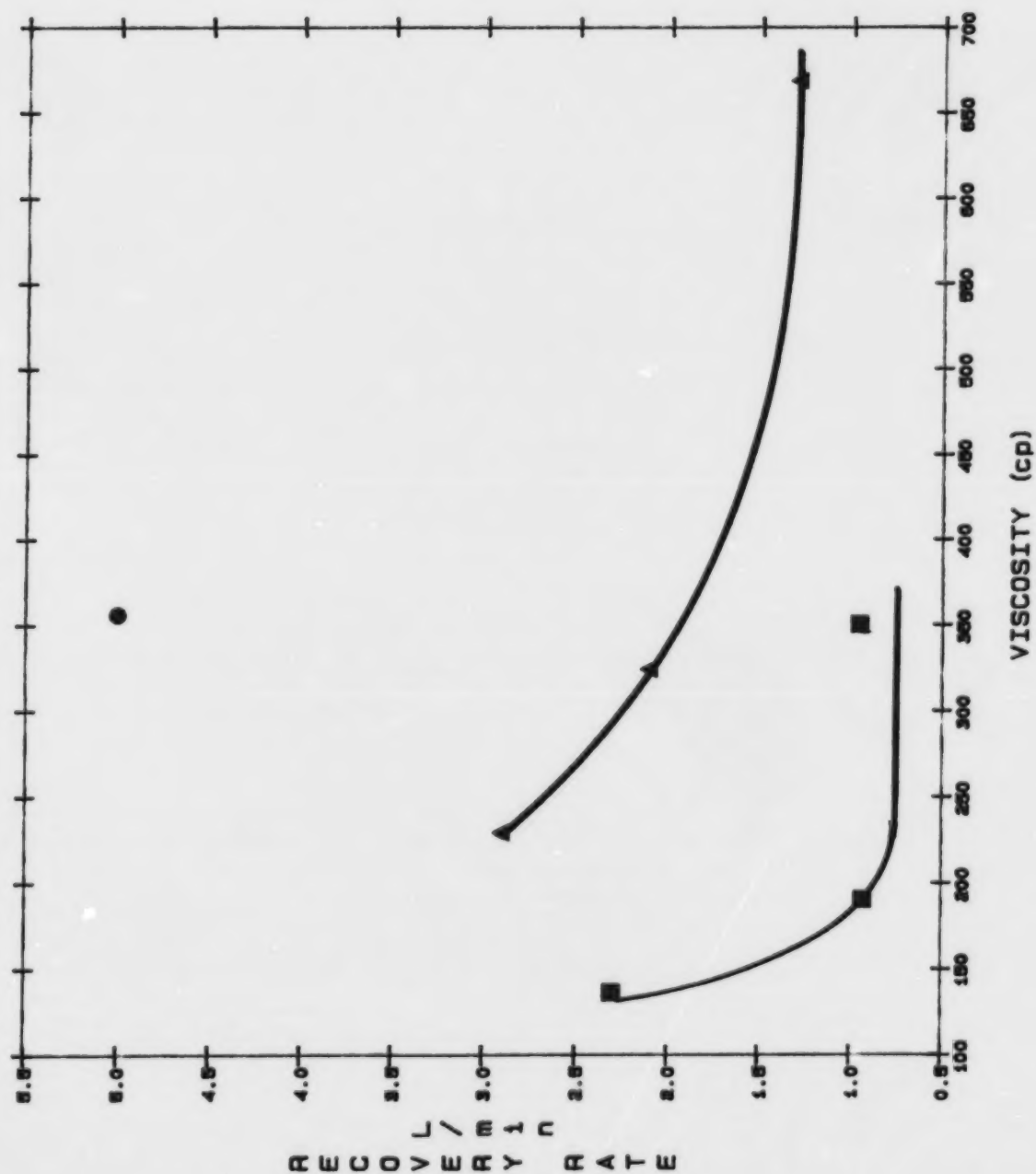
Testing done with Elastol showed that its application resulted in a dramatic increase in viscosity and in recoverability. A slick treated with 2000 ppm was of sufficient viscoelasticity that its recoverability exceeded the capacity recovery rate of a Morris MI-2C skimmer. A slick of Norman Wells crude treated 4000 ppm of Elastol proved to be insufficiently thick to propagate burning.

ACKNOWLEDGEMENTS

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Figure 13. EFFECT OF TREATMENT ON RECOVERY RATES



ELASTOL TREATED
UNTREATED
DEMOUSSIFIER

● ▲ ■

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Laboratory tests of ELASTOLT.M. (Oil Spill Combat Agent)

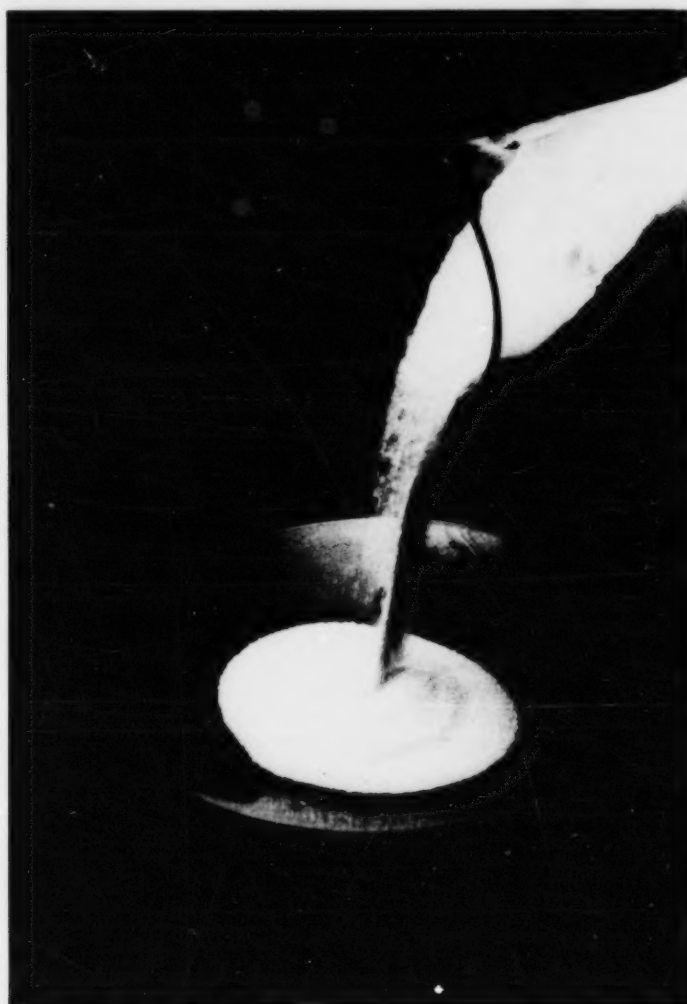
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I. Introduction

ELASTOLT.M.* was developed by GTA with the assistance of BASF. It is manufactured in the form of a white powder with particle sizes between 100 μm and 1000 μm (Fig.1).

Fig.1: The powder form of ELASTOLT.M. simplifies application.



* in USA registered trademark of General Technology Applications (GTA) Inc., Manassas, Virginia; in other countries of Elastogran Polyurethane GmbH, a company of BASF group

The powder contains about 50% by weight of Polyisobutylene (PIB) of extremely high molar mass ($M_w \sim 6 \cdot 10^6$ g/mol). PIB is a non-toxic polymer that only consists of carbon and hydrogen atoms.

Fully extended the polymer chain would reach a length of about 17 μm . Granules of polymeric material are coated with water-insoluble $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ salt and Calciumstearate in order to obtain an easily spreadable, non-agglomerating powder that floats on water. Only the PIB-component is soluble in oil. When dissolved the macromolecules give rise to a distinct viscoelasticity as well as to a drastic increase in the elongational viscosity of the solution even at PIB concentrations of only a few hundred ppm.

These properties make ELASTOLT.M. a very interesting oil spill treating agent [1]. The performance of skimmers is improved, the resistance to spreading and break-up is greater, and the speed of collecting barriers can be increased.

In this work we report laboratory tests with ELASTOLT.M. applied to different oils at various concentrations. In Table 1 the fractionated oils and crude oils used in the investigation are listed. η_0 is the zero shear rate viscosity of the oils at 25 °C.

Table 1: List of oils and their zero shear rate viscosities η_0 at 25 °C.

fractionated oils	η_0 [mPa·s]
petroleum	1.42
fuel oil	3.65
diesel oil (Columbia diesel)	6.9
spindle oil	7.0
transmission lubricant/petroleum 1/1 (mixture)	10.5
transformer oil	13.0
MARCOLT.M. 82 (Exxon)	21.6
fine mechanics lubricant	34.3
vacuum pump oil	190
transmission lubricant	713

crude oils	η_0 [mPa·s]
Quaibo	4.6
Arabmed	18.0
Venezolana/Quaibo 61/39 (mixture)	70.0

II. Rheological properties of ELASTOL^{T.M.} oil solutions

1. Dependence of the solution viscosity on the type of oil

The oils listed in Table 1 were treated with both 2 000 ppm and 10 000 ppm (0.2 and 1% by weight) ELASTOL^{T.M.}. The solutions were produced by rolling the powder-oil mixtures in closed glass bottles at about 120 rpm and 23 °C for a time period of 30 to 70 hours.

The viscosities of the resulting solutions were determined by means of a high precision Couette Rheometer (Contraves LS 30).

In Figure 2 and Figure 3 the relative viscosities (= ratio of solution viscosity and oil viscosity) are plotted versus the logarithm of the oil viscosity for 2 000 ppm and 10 000 ppm powder, respectively. They increase with increasing powder concentration. It is also seen that the relative viscosity increase due to ELASTOL^{T.M.} becomes smaller with increasing viscosity of the oil. It is interesting to note that for the 1/1 mixture of petroleum and transmission lubricant as well as for the crude oils, the relative viscosities are significantly smaller compared to fractionated oils of similar viscosity. A possible explanation for the observed effect might be the reduction of the coil extension in the oil mixtures due to changes in the average polymer-solvent interaction.

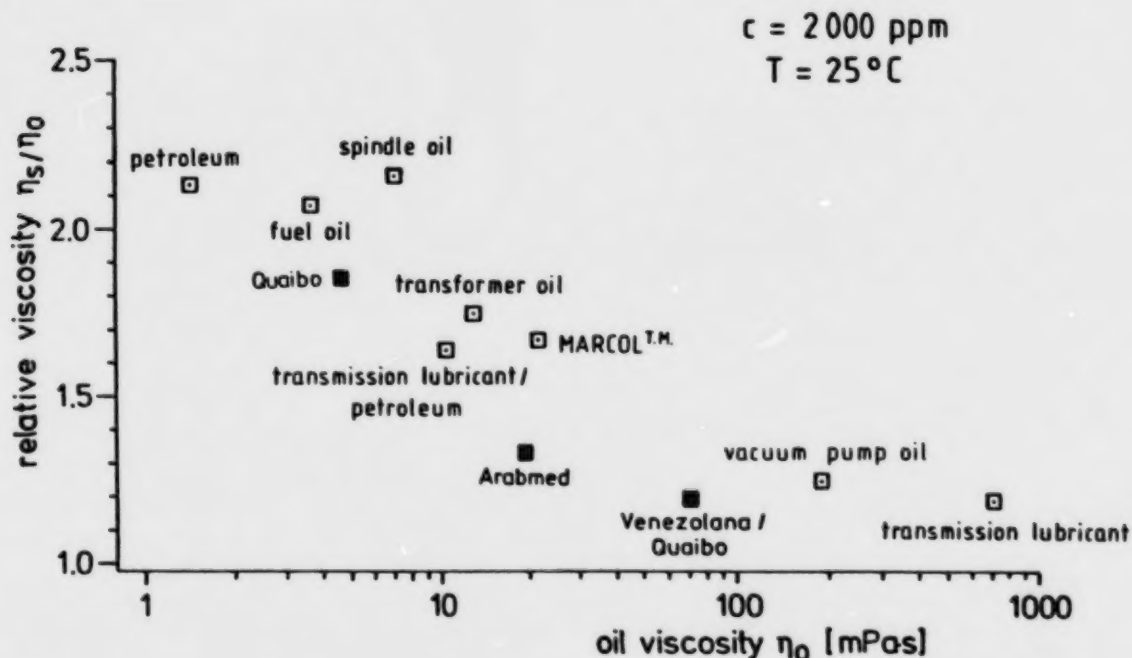


Fig.2: Relative viscosities η_r for various oils as obtained after rolling powder oil mixtures with an ELASTOL^{T.M.} concentration of 2 000 ppm at 25 °C. Open symbols represent fractionated oils, full symbols crude oils.

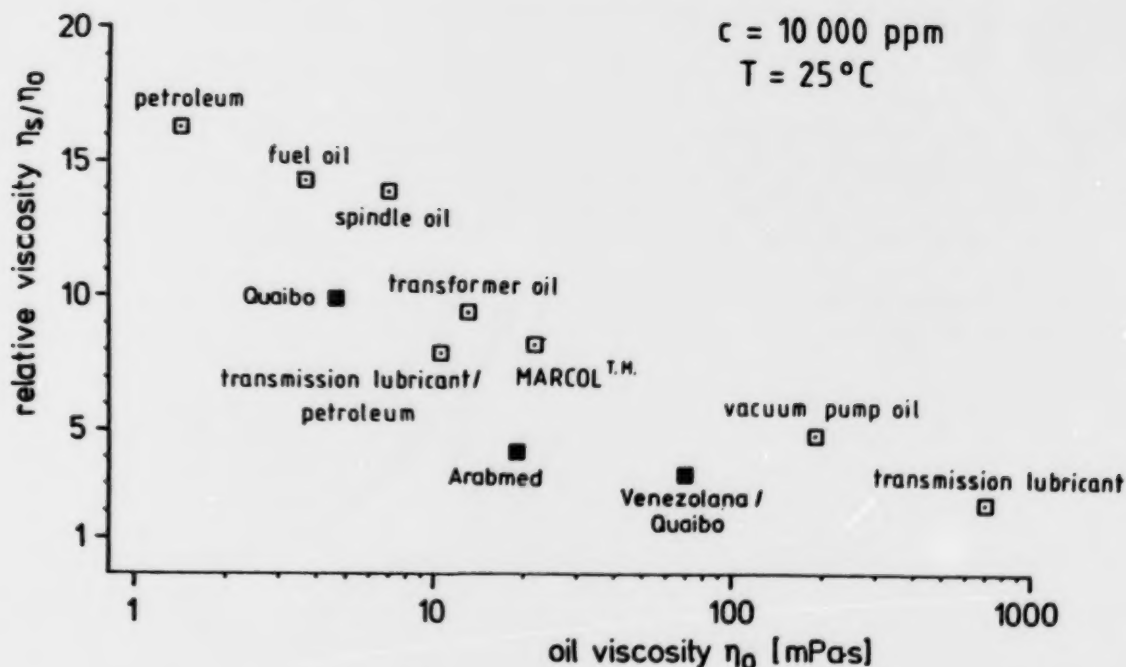


Fig.3: Same as Fig.1 for an ELASTOL^{T.M.} concentration of 10 000 ppm.

2. Dependence of solution viscosity on powder concentration

Zero shear rate viscosities of the solutions (denoted by η_s) were measured at various concentrations for petroleum and fuel oil. For this purpose base solutions having 6 000 ppm ELASTOL^{T.M.} were prepared and subsequently diluted by adding solvent. The resulting data are shown in Figure 4.

The experimental results are nicely described by a polynomial of order 2 (full lines) as proposed by Huggins [2]:

$$\eta_s = \eta_0 (1 + [\eta]c + k_H [\eta]^2 c^2) \quad , \quad (2)$$

$[\eta]$ being the intrinsic viscosity and k_H the Huggins constant.

The pronounced quadratic increase of η_s versus concentration indicates that the coils of the dissolved PIB molecules overlap in the concentration range under consideration. The decrease of both $[\eta]$ and k_H in going from petroleum to fuel oil is due to a reduction in the coil diameter.

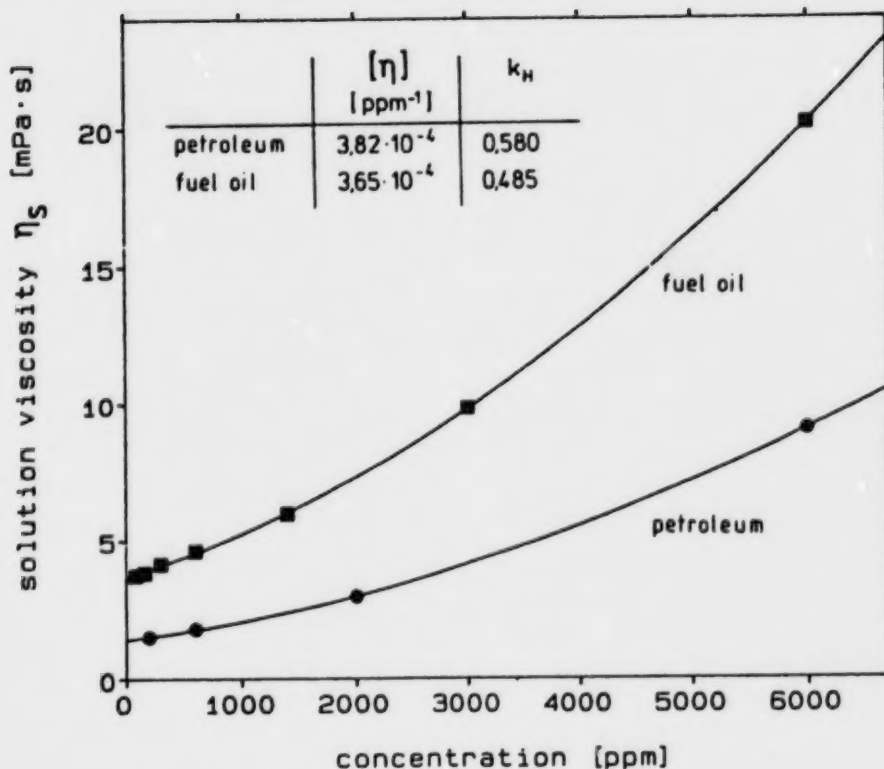


Fig.4: Solution viscosity η_s versus ELASTOLT^{T.M.} concentration for petroleum and fuel oil. Full lines represent the fit by the Huggins equation (see text) using the parameters given in the inserted table.

3. Viscoelasticity of ELASTOLT^{T.M.} solutions

The solutions were submitted to small amplitude oscillatory shear in a rotational rheometer using bi-cone geometry (see Fig.5). The radius was $R = 25$ mm and the gap angle $\alpha = 3.8^\circ$. Angular frequencies $\omega = 2\pi f$ (f frequency of the oscillation) in the range of 0.2 to 18 s^{-1} and a constant shear amplitude $\gamma = 0.5$ were used.

The resulting shear stress σ_{21} is oscillating at the same frequency but is phase shifted compared to the shear strain γ [3] (see Fig.6). The direct output of the measurements are the storage modulus G' and the loss modulus G'' as functions of the angular frequency ω . In our experiments the contribution of inertia forces to G' has been corrected for analytically.

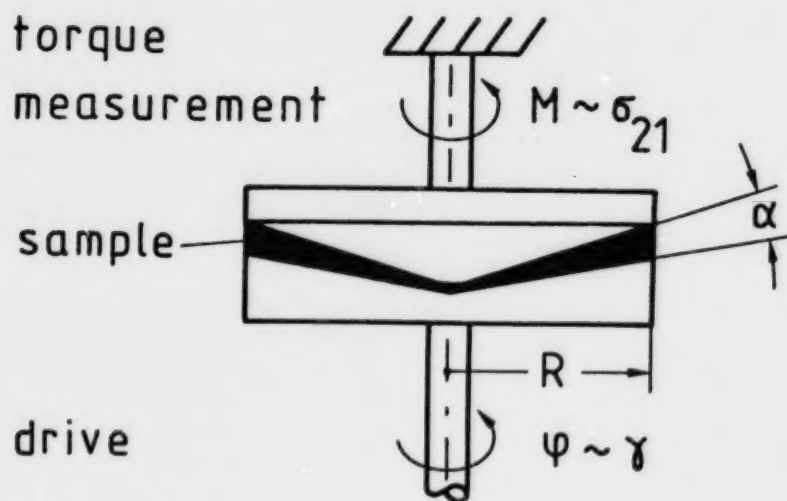
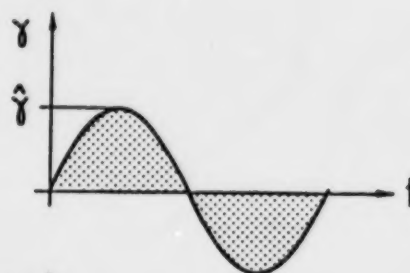


Fig.5: Schematic drawing of the bi-cone geometry used for small amplitude oscillatory shear.

shear strain γ :

$$\gamma = \hat{\gamma} \sin \omega t$$



shear stress σ_{21} :



$$\sigma_{21} = \hat{\gamma} [\underbrace{G' \sin \omega t}_{\text{storage modulus}} + \underbrace{G'' \cos \omega t}_{\text{loss modulus}}]$$

Fig.6: Decomposition of the phase shifted oscillating shear stress into two components yields the storage modulus G' and the loss modulus G'' .

As an example Figure 7 shows the measured dynamic moduli of a 16 000 ppm solution of ELASTOLT.M. in petroleum. The pronounced viscoelasticity of the solution is evident from the fact that besides the loss modulus a distinct storage modulus can be measured. The ratio G'/G'' increases with growing angular frequency.

The viscosity $|\eta^*|$ represented by the full symbols is calculated from the moduli according to

$$|\eta^*| = \frac{1}{\omega} \sqrt{G'^2 + G''^2} \quad (4)$$

This quantity is very close to the value of the viscosity in steady shear flow if ω is equal to the shear rate [4]. Thus, the decrease of $|\eta^*(\omega)|$ with increasing angular frequency reflects the non-Newtonian behaviour of the solution, viz. the shear viscosity decreases with increasing shear rate.

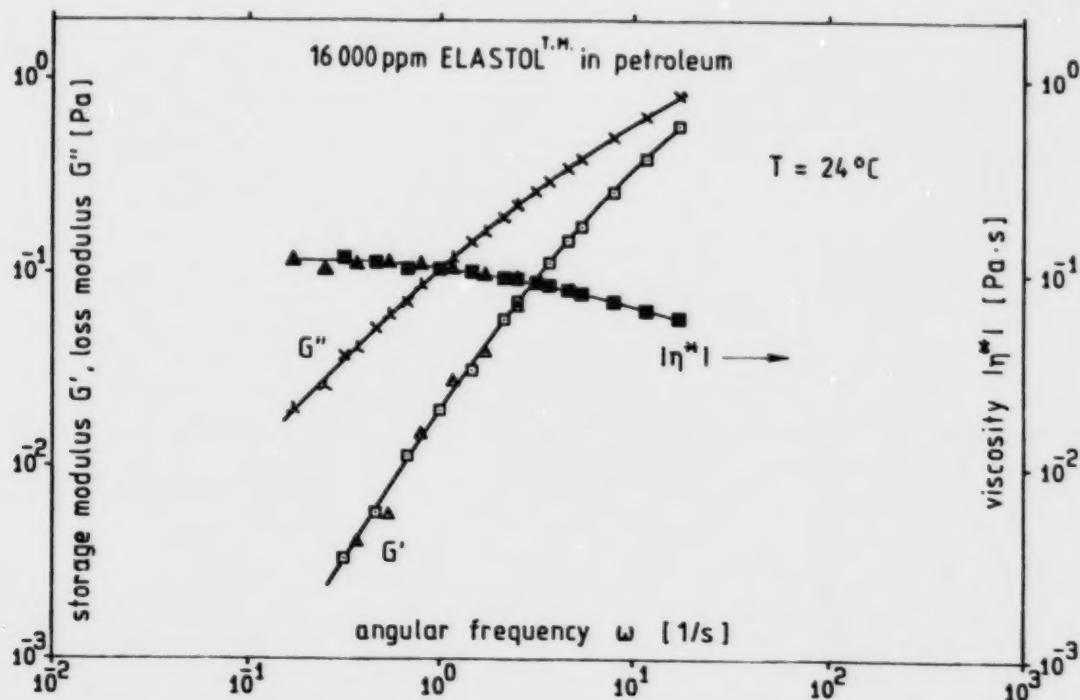


Fig.7: Storage and loss moduli (open symbols) and viscosity (full symbols) versus angular frequency of an ELASTOLT.M. solution in petroleum at 16 000 ppm and 24 °C.

Figure 8 shows the concentration dependence of the moduli in diesel oil. The pure oil (full circles) is Newtonian and does not have a measurable storage modulus. With increasing ELASTOLT.M. concentration the storage modulus grows stronger

than the loss modulus. For $\omega = 1 \text{ s}^{-1}$ (0.13 Hz) a fourfold increase in concentration (4 000 ppm to 16 000 ppm) yields a G'' growth of less than a factor of 20 whereas the storage modulus increases approximately 100-fold. As a result, the ratio G'/G'' at a given frequency (cf. Table 3), taken as a quantitative measure of the viscoelasticity, increases considerably. A comparison of the dynamic moduli for a constant ELASTOL^{T.M.} concentration of 2 000 ppm in various oils of different viscosities is shown in Figure 9.

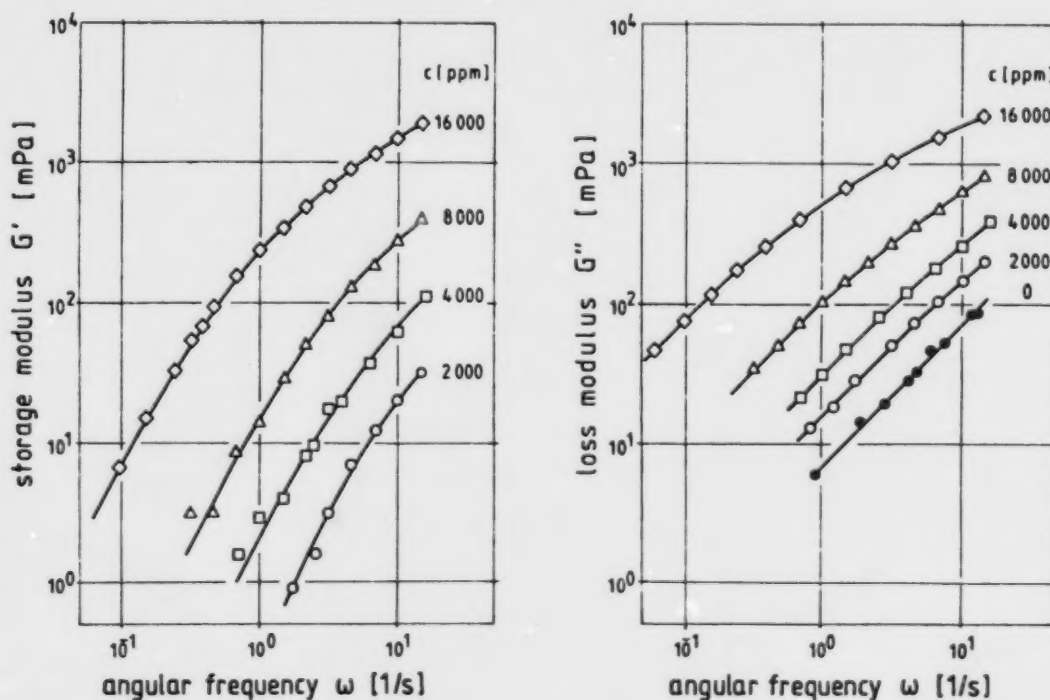


Fig.8: Storage modulus (left diagram) and loss modulus (right diagram) versus angular frequency of ELASTOL^{T.M.} solutions in diesel oil at various concentrations and 24 °C. The pure oil does not have a measurable storage modulus.

The behaviour of long polymer chains dissolved in a viscous fluid (PIB macromolecules dissolved in oil in our case) can be understood as follows: at rest the molecules have a random coil like equilibrium conformation (left side of Fig.10). In a flow field the random coils immobilize part of the solvent giving rise to the observed viscosity increase with increasing polymer concentration.

During flow the molecule attains an ellipsoidal conformation (right side of Fig.10) and will partially be oriented parallel to the direction of flow. This deformation of the coil, however, is reversible. When the flow is stopped the molecule will re-establish its equilibrium conformation.

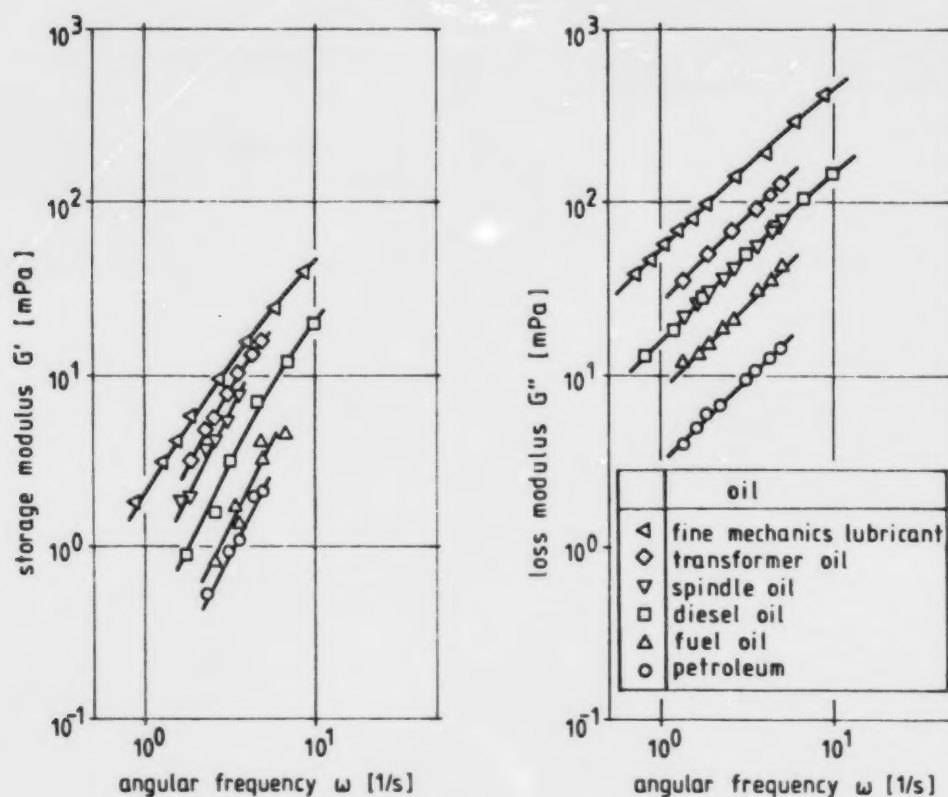


Fig.9: Storage modulus (left diagram) and loss modulus (right diagram) versus angular frequency for ELASTOL^{T.M.}

4. Drawability (elongational viscosity) of ELASTOL^{T.M.} solutions

One of the most striking effects of ELASTOL^{T.M.} dissolved in oil is the dramatic increase in resistance to elongational flows. When the solution is stretched the PIB molecules are oriented which yields an elongational viscosity greater than three times the shear viscosity [5]. This behaviour is best demonstrated in the ductless siphon test [6] (Fig.11).

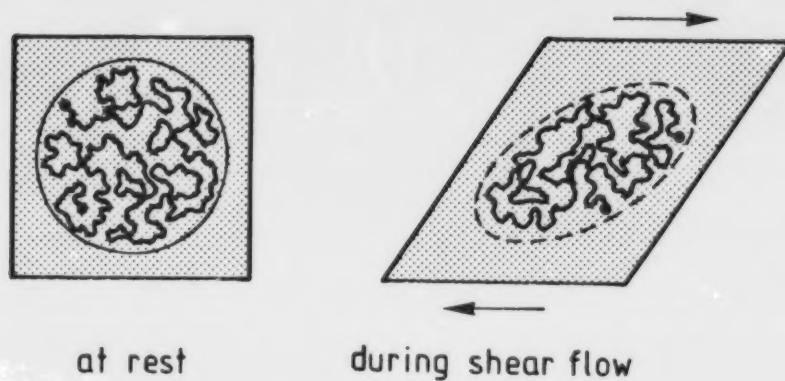


Fig.10: Equilibrium conformation (random coil) at rest and deformed state during flow of a macromolecule in solution (schematic).

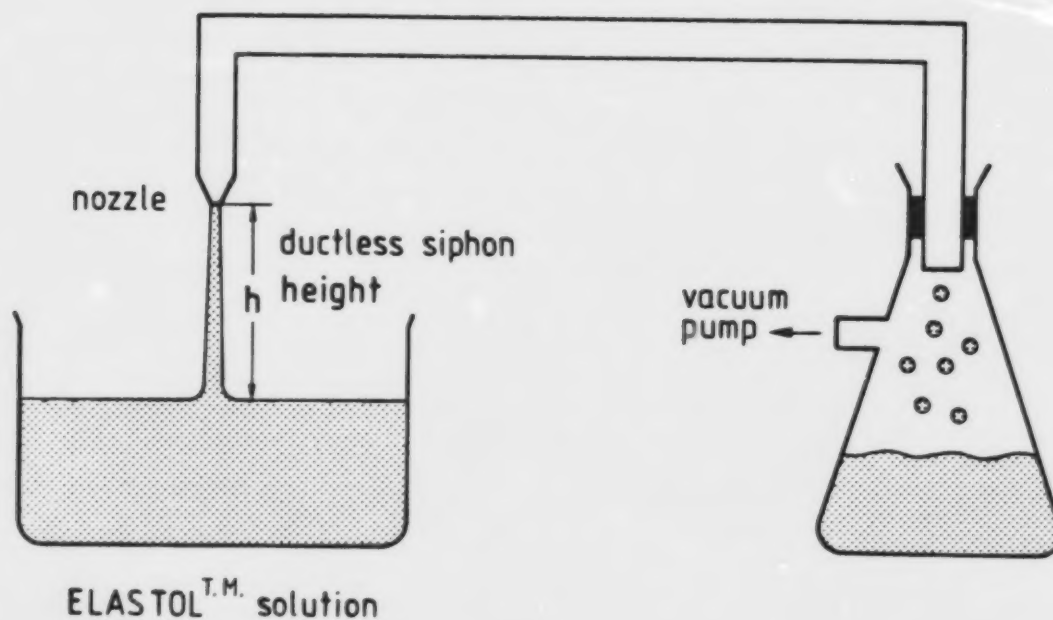


Fig.11: Schematic drawing of the ductless siphon test method. The ductless siphon height is gradually increased until break of the filament at $h_{\max}$.

A pipe being connected to a vacuum pump carries a nozzle at its other end. The solution is contained in a beaker. When the nozzle is brought into contact with the meniscus of the solution the latter is sucked out of the beaker. The distance h between nozzle and solution meniscus is increased either by slowly lowering the container position or just due to the decreasing meniscus height for a fixed beaker position. The solution will still flow upward until at a maximum ductless siphon height $h_{\max}$ the filament breaks.

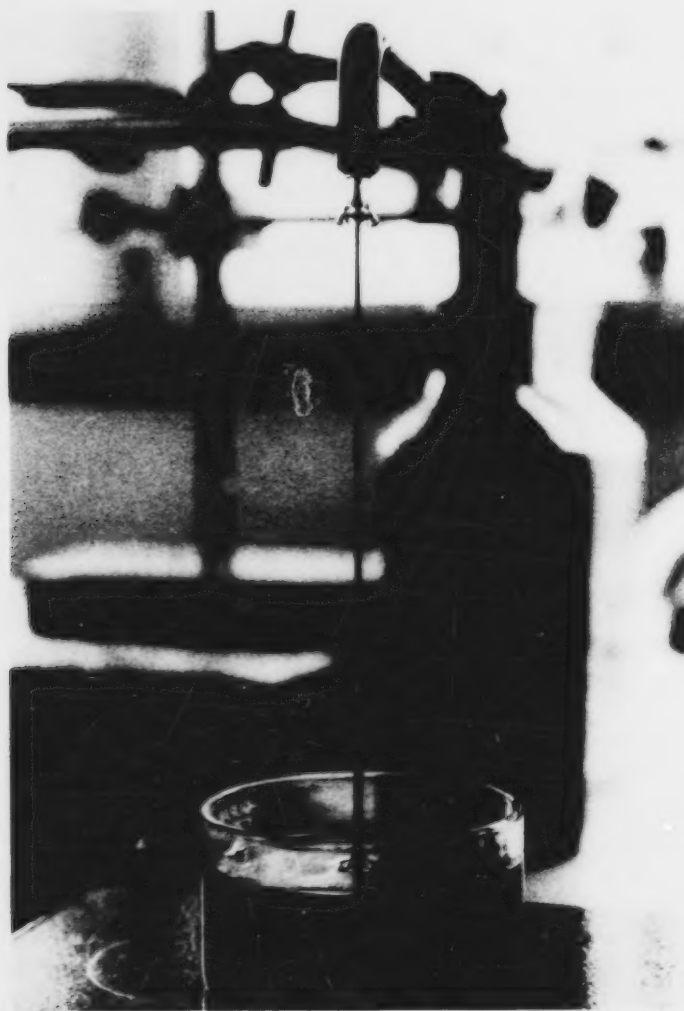


Fig.12: Ductless siphon test on a 4 000 ppm solution in fine mechanics lubricant. Nozzle diameter 1 mm.

For an untreated oil, in general, the maximum ductless siphon height will be in the order of 1 mm. With ELASTOL^{T.M.} $h_{\max}$ is much greater and may reach values of half a meter or more. This behaviour is of tremendous importance for the performance of collecting devices used for oil spill combat.

A photograph of the spinline in the ductless siphon test is shown in Fig.14 for a 4 000 ppm solution in fine mechanics lubricant (with red dye) and a nozzle diameter of 1 mm. The distance between the nozzle and the solution meniscus was 20 cm.

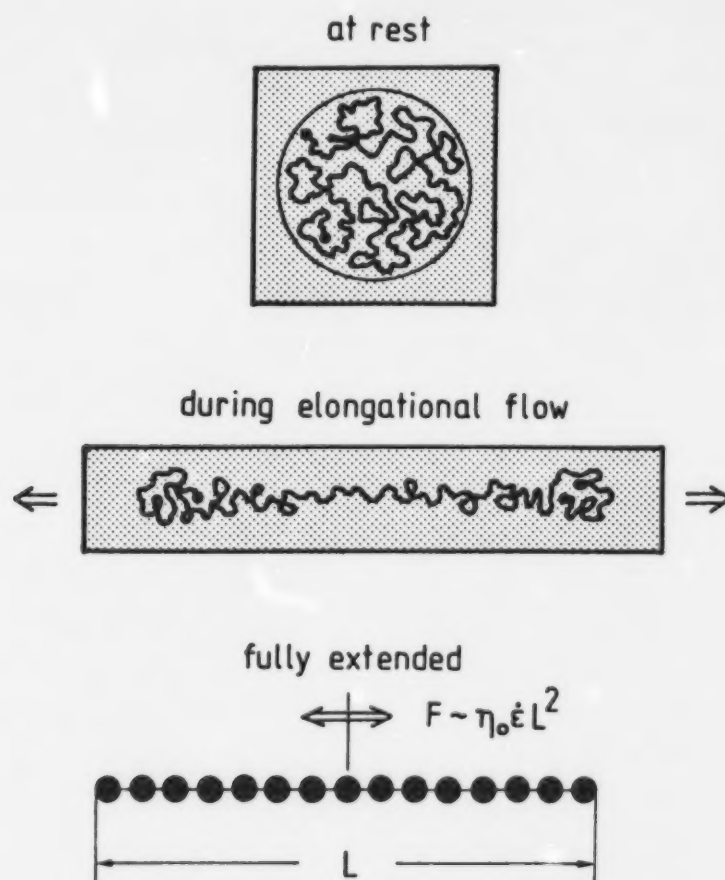


Fig.13: Stretching of the polymer chain when the solution is subjected to an elongational flow field (schematic).

The physical reason for the high elongational viscosity is schematically depicted in Fig.13. At rest the molecule has a coil like conformation, but in an extensional flow field, the molecule is stretched. The degree of stretching is dependent on the rate of strain of the solution and the duration of extensional flow. The sum of friction forces due to the surrounding solvent molecules has an opposite sign on both sides of the center of mass. Therefore, the extensional forces acting on the molecule are maximal in the middle of the chain and the orientation of chain segments parallel to the direction of strain is most pronounced in that region.

For the extreme case of a fully extended chain (bottom diagram in Fig.13) it is easy to show that the force F acting in the center of the molecule is proportional to the square of

the chain length L , the solvent viscosity η_0 , and the strain rate $\dot{\epsilon}$ [7]. The force F may even become higher than the chemical bond of the backbone. Under that condition the molecule will break [7].

The measured ductless siphon heights $h_{\max}$ of petroleum, fuel oil, and spindle oil versus ELASTOLT.M. concentration are plotted in Figure 14. We observe a monotone increase of $h_{\max}$ with increasing powder concentration in petroleum. For fuel oil and spindle oil, however, $h_{\max}$ goes through a reproducible minimum. It appears that the concentration corresponding to the filament length minimum is shifted to smaller values when the oil viscosity is increased. Most probably this effect is not caused by a minimum in the true resistance of the filament to stretching but by problems in the nozzle flow due to the shear viscosity which increases with concentration.

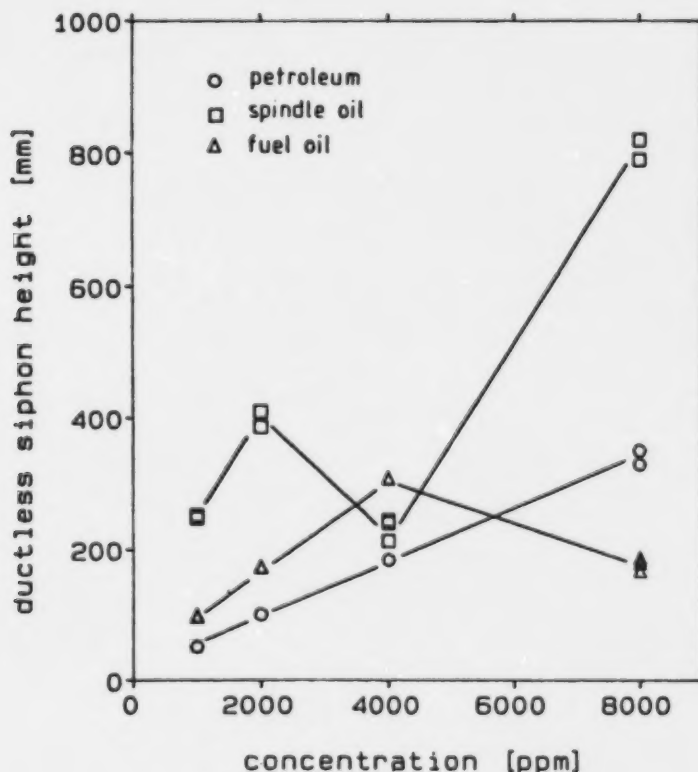


Fig.14: Maximum ductless siphon heights at room temperature for three oils versus ELASTOLT.M. concentration (nozzle diameter 1 mm).

Table 2: Ductless siphon heights $h_{\max}$ at filament break for various oils at an ELASTOLT.M. concentration of 2 000 ppm.

oil	η_0 [mPa·s]	$h_{\max}$ [mm]
petroleum	1.42	100
fuel oil	3.8	187
spindle oil	7.0	380
transformer oil	13.0	471
fine mechanics lubricant	34.3	805
petroleum + SEPAROLT.M. AF 27	-	99

Table 2 gives a compilation of the measured $h_{\max}$ values in various oils for a constant ELASTOLT.M. concentration of 2 000 ppm. The maximum ductless siphon height strongly increases with increasing oil viscosity. Therefore, the higher the oil viscosity, the lower the concentration of ELASTOLT.M. required to obtain a given value of $h_{\max}$.

As already mentioned, the drawability of ELASTOLT.M. solutions is an exclusively physical phenomenon. The application of chemical additives (for instance emulsion breakers) should have no influence on the ductless siphon heights. This was experimentally verified for petroleum treated with 2 000 ppm ELASTOLT.M. and 100 ppm SEPAROLT.M.* AF 27 (emulsion breaker). The same value of $h_{\max}$ as given in Table 4 for the pure petroleum was observed.

The drawability increase due to ELASTOLT.M. is of great advantage in collecting oil floating on a water surface. As shown in Fig.15 a-d, fine mechanics lubricant treated with 4 000 ppm ELASTOLT.M. can completely be removed from a water surface by means of a ductless siphon. A field test with crude oil from ERM (= refinery Mannheim) spread on water in a training basin gave the following results for a vacuum skimmer: In the case of untreated oil 90% water and only 10% oil were collected. After the application of 6 000 ppm ELASTOLT.M. powder 95% oil and only 5% water were collected [8]. Fig.16 shows that the oil film is pulled from the water surface without rupture and can easily be sucked by the vacuum skimmer over a distance of about 15 cm.

* registered trademark of BASF Aktiengesellschaft

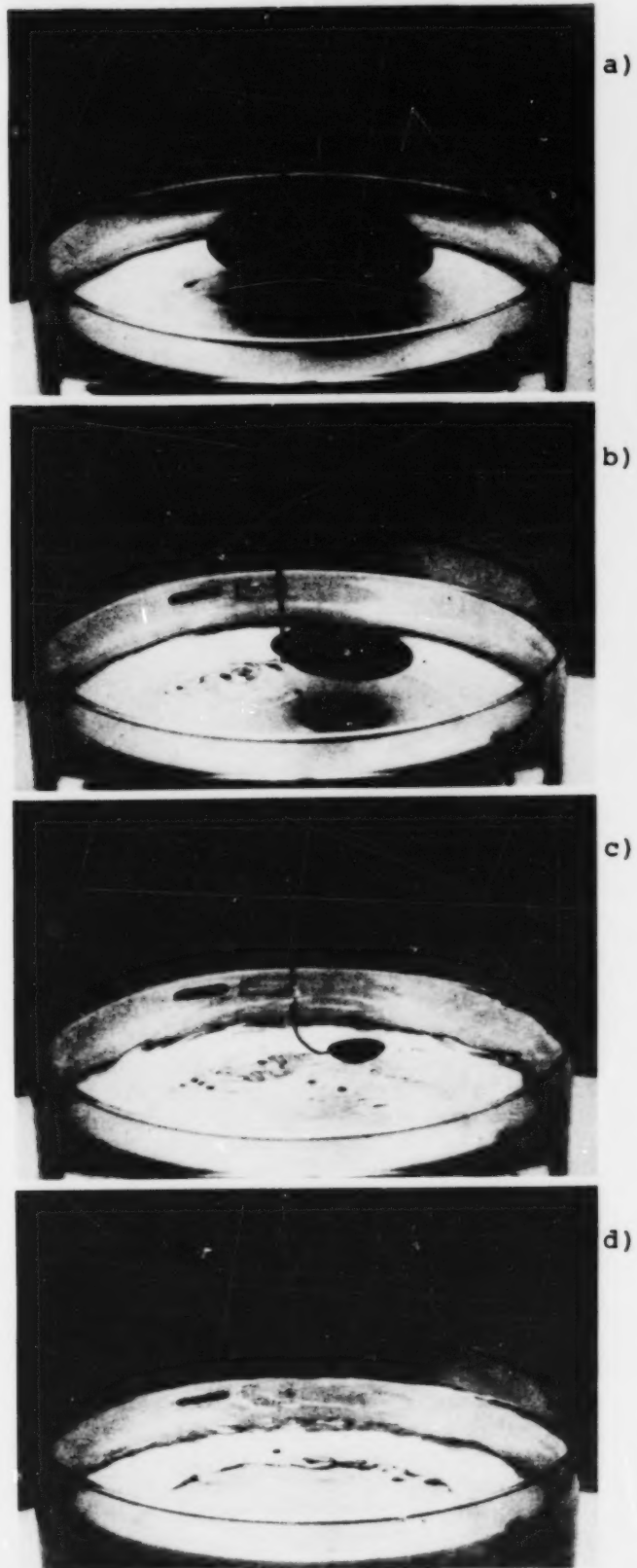


Fig.15: Fine mechanics lubricant treated with 4 000 ppm ELASTOLT.M. is easily removed from a water surface by means of a ductless siphon.

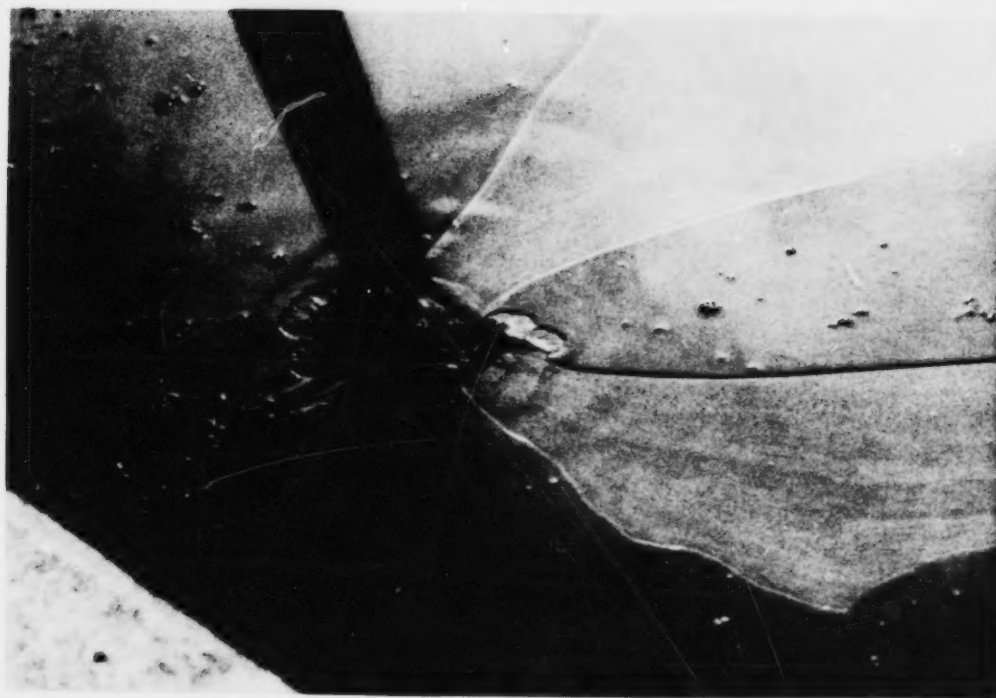


Fig.16: Example of the improved performance of a vacuum skimmer in collecting crude oil (ERM) from a water surface [8].

5. Consequences of ELASTOLT.M. on droplet formation

Fig.17 shows schematically the break up of an oil droplet into two smaller droplets due to an elongational flow field. Once a neck is formed the neck is elongated until break of the strap. The formation of smaller droplets continues until the rheological forces can no longer overcome the stabilizing effect of the interfacional tension.

With dissolved macromolecules, however, it is possible to prevent the formation of very small droplets [6]. Here, the limiting drop size is governed by the resistance of the strap to stretching. When the elongational viscosity in the neck is increased the break up process will come to an end at a bigger droplet size.

The consequence for oil/water mixtures is demonstrated by Fig.18. Two glass bottles were partially filled with water. In the right bottle pure Heizöl was used whereas in the left bottle the oil was treated with 10 000 ppm ELASTOLT.M.. The closed bottles were shaken by hand for a given time period. After a settling time of about 10 seconds we observe in the right bottle a milky emulsion of very small oil droplets in

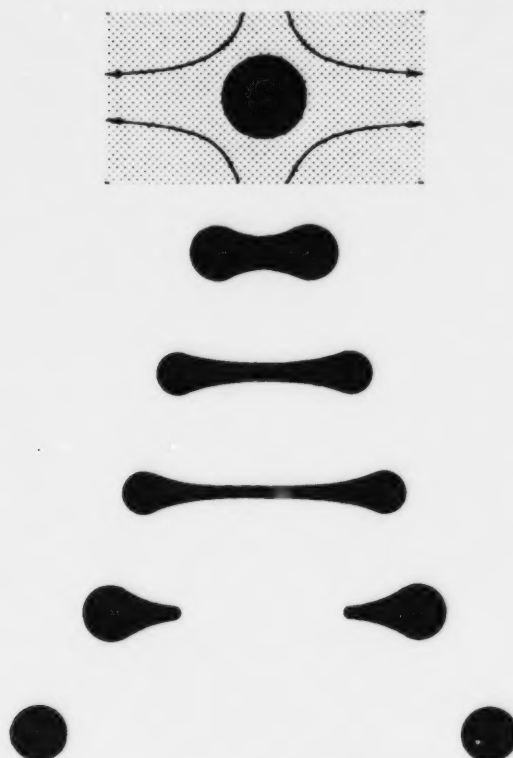


Fig.17: Formation of smaller droplets in an elongational flow field (schematic).

in water. The water and oil phases are hardly separated. In the case of the ELASTOL^{T.M.} treated oil (right) we get a coarse emulsion by shaking. The separation of water and oil is nearly complete after 10 seconds.

III. Dissolving behaviour of ELASTOL^{T.M.} powder

The efficiency of ELASTOL^{T.M.} in treating oil spills is strongly dependent on the dissolving speed of the powder after being spread onto oil layers floating on water. As a measure of the effective solution concentration we determined the oil solution viscosity as a function of time.

Figure 19 shows the result as measured for fuel oil at a powder concentration of 10 000 ppm. In a first test series depicted by full circles the dissolving of ELASTOL^{T.M.} took place without any agitation. Obviously, in that case a significant increase of the solution viscosity is only observed at times greater than 100 hours.

In a second series of tests a gentle agitation was attained by stirring. A schematic drawing of the arrangement is shown in Figure 20. The rotary speed of the stirrer was 0.5 revolutions



Fig.18: Diesel oil/water mixtures after shaking and a settling time of 10 seconds. Pure oil (right), oil treated with 10 000 ppm ELASTOL^{T.M.} (left).

per second. As can be seen from Fig.19 the gentle agitation drastically increases the speed of dissolving (open circles). A significant increase in the oil solution viscosity was observed after only 0.5 hours.

By comparing the viscosities determined for solutions prepared by rolling and the results obtained in the dissolving tests with gentle stirring (neglecting the influence of partial evaporation) we can evaluate the time necessary to dissolve an effective concentration of 2 000 ppm ELASTOL^{T.M.} out of a total powder concentration of 10 000 ppm. The necessary times are plotted in Figure 21 as a function of the oil viscosities η_0 (double-log representation). The increasing dissolving time is approximately proportional to the oil viscosity.

IV. Water/crude oil emulsions

The formation of extremely stable water-in-crude oil emulsions, often called "chocolate mousse", is a major problem in combatting oil spills at sea. These emulsions are highly viscous and their water content can be as high as 90%. They are difficult to collect and even more difficult to dispose of. According to Bredie et al. [9] the formation of these mousses depends on the presence of both wax and asphaltenes in the crude oil. These authors suggest that wax/asphaltene crystals may stabilize small water droplets in the oil, leading to a dramatic increase in viscosity.

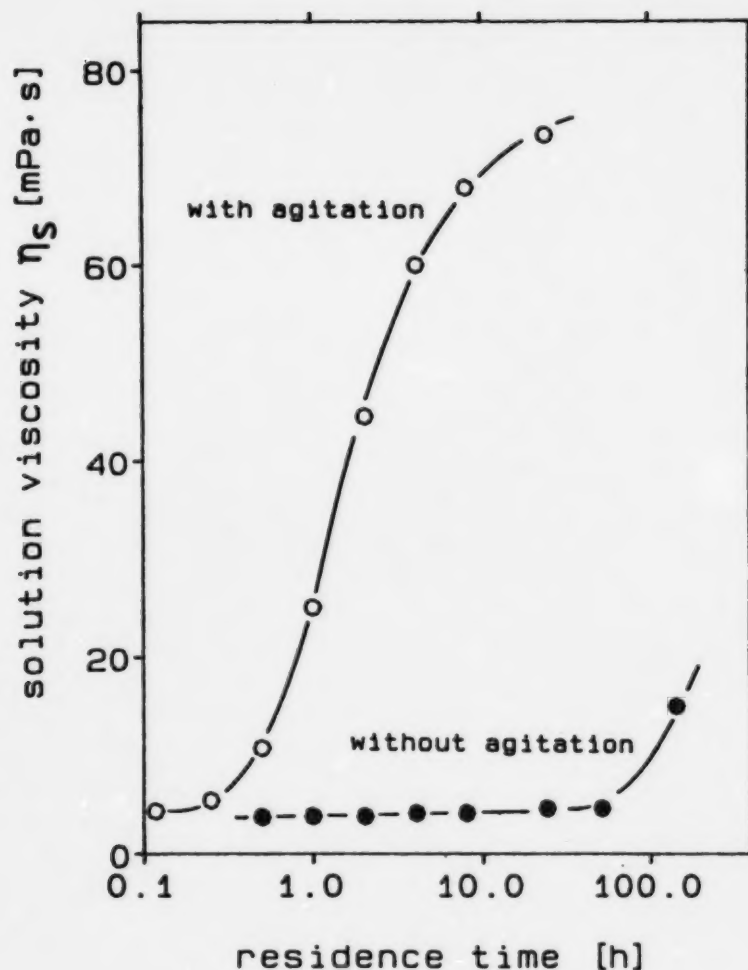


Fig.19: Solution viscosities of fuel oil layers (5 mm thickness) floating on top of water versus time elapsed after application of ELASTOL^{T.M.} by spraying (concentration 10 000 ppm related to the total weight of oil) with (open circles) and without (full circles) gentle stirring.

In order to produce "chocolate mousse" on a laboratory scale we performed experiments with various water-in-oil mixtures. In one series of tests different oil-water mixtures were treated with a shaker ("red devil") in closed bottles for 15 min. As expected the formation of a stable emulsion could not be observed for dewaxed and deasphaltenized oils like transformer oil or MARCOL^{T.M.} 82. After a settling time of several minutes the water and oil phases separated. For the crude oils listed in Table 2, however, stable water-in-oil emulsions were easily produced by shaking. Even after a settling period of 24 hours no phase separation was observed.

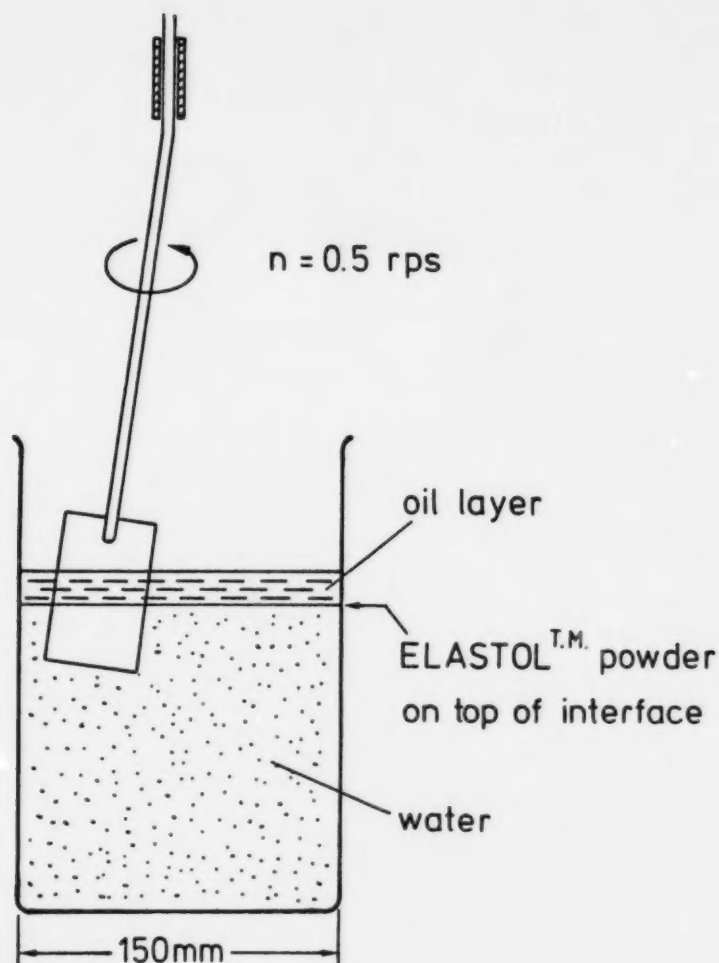


Fig.20: Experimental arrangement for the dissolving tests with stirring.

The most stable "mousse" could be produced with Arabmed ($\eta_0 = 18 \text{ mPa}\cdot\text{s}$) for which a sudden rise in viscosity of the emulsion was observed with increasing water content. For a 70% water-in-oil emulsion a viscosity of $20 \text{ mPa}\cdot\text{s}$ was measured, whereas for 80% (90%) water content 6100 (8100) $\text{mPa}\cdot\text{s}$ were observed. The latter "mousse" appears stiff, viz., it has a yield stress which is strong enough to prevent deformation by gravitational forces.

When the same experiments were repeated on Arabmed treated with 2 000 ppm ELASTOL^{T.M.} the sudden rise in viscosity in going from 70% to 80% water content was reduced by at least a factor of 4. For both 80% and 90% water content viscosities of about $1500 \text{ mPa}\cdot\text{s}$ were measured indicating that ELASTOL^{T.M.} improves the pumpability of "chocolate mousse".

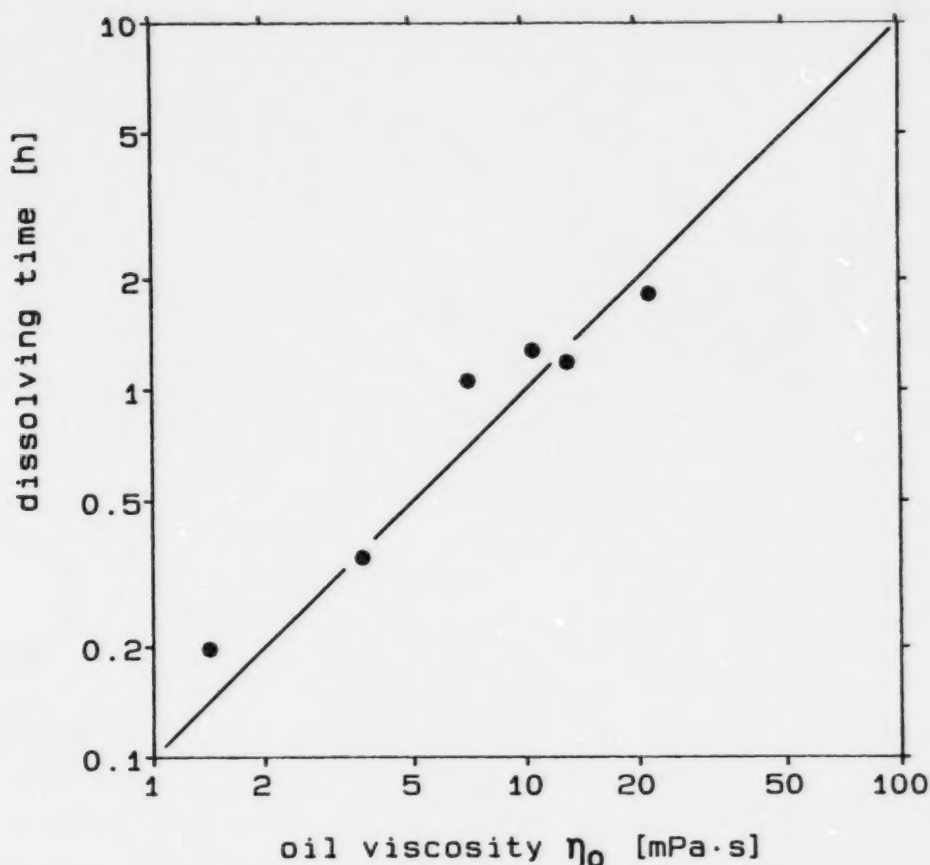


Fig.21: Dissolving time for 2 000 ppm ELASTOL^{T.M.} out of an initial powder concentration of 10 000 ppm versus oil viscosity. The effect of partial evaporation during stirring is neglected here.

Fig.22 demonstrates that without ELASTOL^{T.M.} a stiff and stable emulsion with yield stress forms. When treated with ELASTOL^{T.M.}, however, the Arabmed/water mixture was fluid even at very low shear stresses and had to be kept in a container. Also a tendency to phase separation between water and oil was evident.

In order to simulate the formation of "chocolate mousse" from crude oil layers floating on water more realistically, the apparatus schematically depicted in Fig.23 was used. Here the fluid was repeatedly picked up by a bucket-wheel and subsequently poured out onto the surface. In this arrangement the formation of stable emulsions was observed after stirring for less than 4 hours (see Fig.24). After 4 hours the "chocolate mousse" formed with untreated Arabmed had a viscosity of 2000 mPa·s.

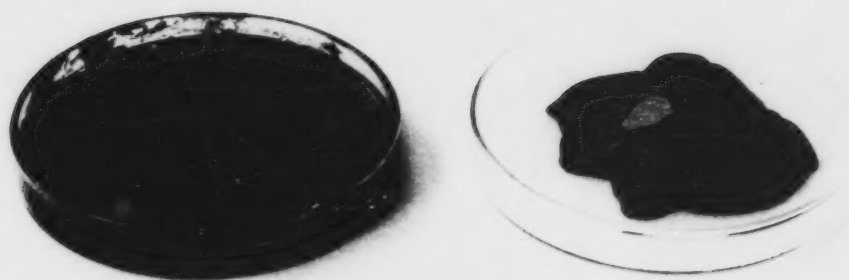


Fig.22: Stiff "chocolate mousse" obtained by shaking Arabmed with 90% water for 15 min in the red devil (right). Crude oil treated with 2 000 ppm ELASTOL^{T.M.} before shaking (left).

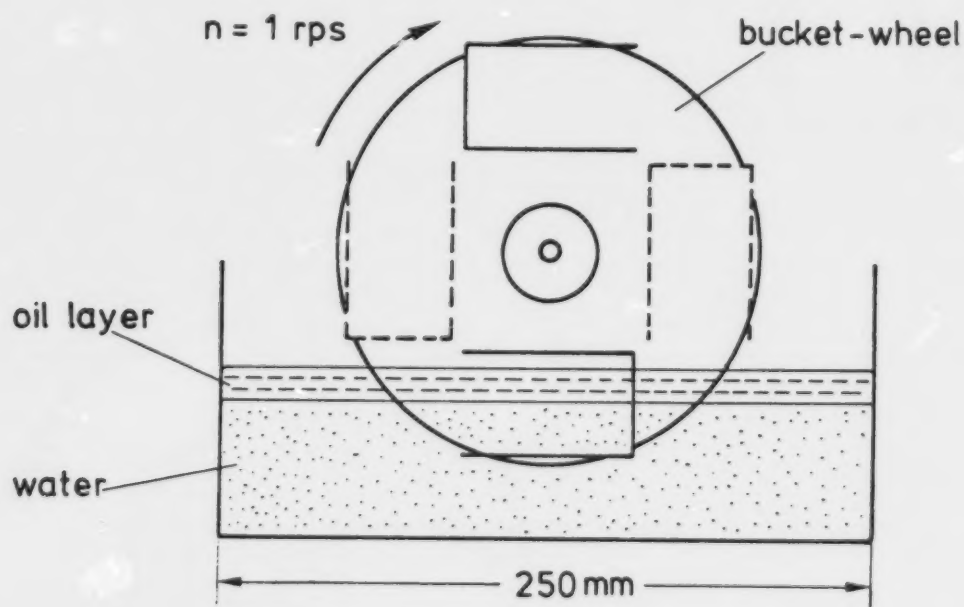


Fig.23: Experimental arrangement for the formation of "chocolate mousses" from crude oil layers floating on water.



Fig.24: "Chocolate mousse" obtained with Arabmed in the bucket-wheel arrangement.

Table 3: Viscosities for "chocolate mousse" formed with Arabmed in the bucket-wheel arrangement (shear rate 2 s^{-1}).

stirring time [h]	residence time [h]	η_0 [mPa·s] untreated crude oil	η_0 [mPa·s] with 2 000 ppm ELASTOLT.M.
4	4	2 000	1 400
8	32	7 800	2 000
12	100	12 200	2 700
16	104	5 400*	

* Addition of 2 000 ppm ELASTOLT.M. to the "chocolate mousse" obtained from untreated Arabmed after 100 hours .

In addition, the bucket-wheel arrangement clearly shows the influence of evaporation. In Table 3 the emulsion viscosities measured after various stirring and evaporation periods are listed.

Stirring intervals of 4 hours and various rest periods have been applied. The first column gives the total stirring time and the second column the total residence time of Arabmed in the bucket-wheel test. For the untreated crude oil the first stirring interval yields a "chocolate mousse" of 2 000 mPa·s. With increasing residence time due to evaporation the "mousse" viscosity increased up to 12 200 mPa·s (100 h).

When 2 000 ppm ELASTOLT.M. powder were spread on the "mousse" a drop in the emulsion viscosity to 5 400 mPa·s was observed after another stirring period of 4 hours (last line in Table 6). This means that the pumpability of the emulsion is improved and the advantage of

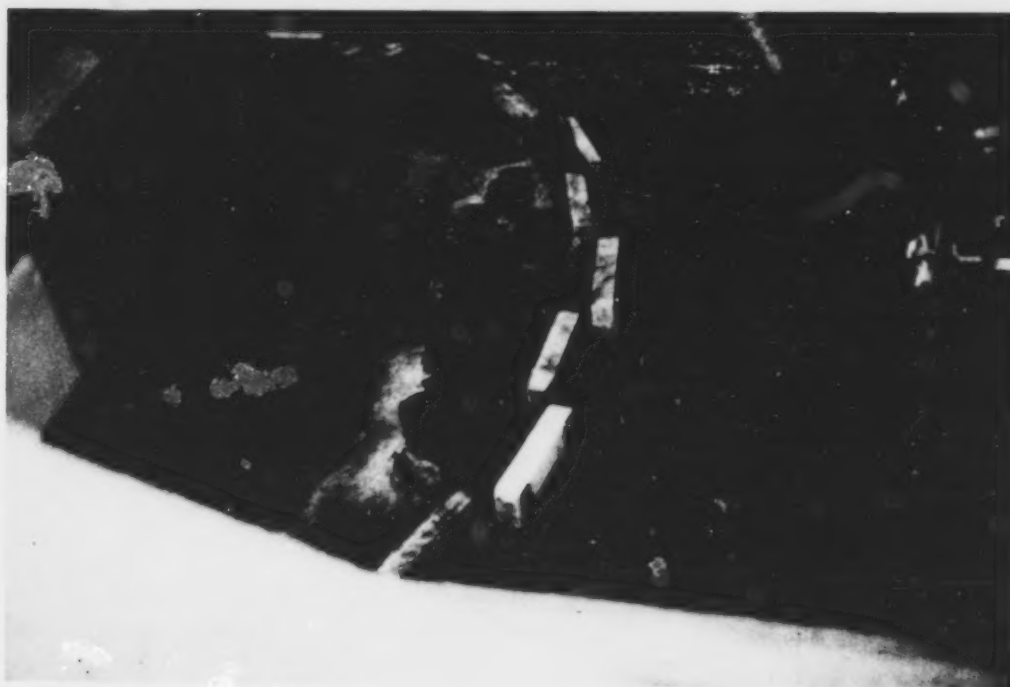


Fig.25: Determination of the critical boom speed at the Berlin Modell Basin [11].

lasticity is obtained by application of ELASTOLT.M. even after the formation of a stiff "mousse". When ELASTOLT.M. was spread on the oil layer at the beginning of the test, viz. before the formation of a "chocolate mousse", the effect of viscosity reduction was even more pronounced (fourth column).

Table 4: Critical boom speed v_c for Marcol 82 ($\eta_0 = 21.6$ mPa·s) at various ELASTOLT.M. concentrations with and without waves (wave length 1.5 m, wave height 0.13 m).

c [ppm]	critical boom speed v_c [m/s]	
	without waves	with waves
0	0.23	0,32 (0.28)
1 000	0.48	0.36
3 000	0.50	0.42 (0.48)
5 000	0.50	
10 000	0.48	

V. Containment tests at the Berlin Model Basin

At the Versuchsanstalt für Wasserbau und Schiffbau (VWS) H.U. Oebius [11] performed containment tests in a 60 m long and 2.5 m wide basin. An amount of 5 l of oil was placed on one side of a boom which could be moved by a towing carriage at variable speeds. This arrangement is shown in Fig.25. The quantity of interest was the boom velocity at which the first droplets appear on the backside of the boom (drainage failure).

In the case of calm water a concentration of only 1 000 ppm ELASTOLT.M. was sufficient to increase the critical velocity from 0.24 m/s to 0.48 m/s for an oil of $\eta_0 = 22$ mPa·s viscosity (MACROLT.M. 82).

With waves of wave length 1.5 m and 0.13 m wave height a critical boom velocity of about 0.30 m/s was measured on MARCOLT.M. 82. The application of 1 000 ppm and 3 000 ppm ELASTOLT.M. increased the critical velocity up to 0.36 and 0.42 m/s, respectively. These numbers are summarized in Table 4.

VI. Summary and Conclusion

In this work rheological properties of ELASTOLT.M. oil solutions are investigated. The most striking rheological effects are the dramatic increase of elasticity and elongational viscosity of the solutions compared to pure oils. This behaviour can be explained on the basis of elastic recoil and orientation by stretching of the PIB macromolecules in the solution. As a practical consequence for oil spill combat the performance of collecting devices is considerably improved. Furthermore, the formation of small oil droplets in agitated oil water mixtures is suppressed, leading to an accelerated phase separation. The dissolving time of ELASTOLT.M. becomes shorter with increasing agitation. Therefore, in practical applications wave motion will improve

dissolving kinetics of the powder. Finally, chocolate mousse with ELASTOLT.M. treated crude oils tends to be unstable, has a reduced water content, and is more easy to pump.

Tank tests [10] have demonstrated that these properties can successfully be transformed to a larger scale. At the present stage quantitative field tests at sea are needed in order to prove the effectiveness of ELASTOLT.M. in a realistic environment. Preparations for such tests are in progress.

Acknowledgement

The authors are indepted to W. Reuther, J. Steidel and Ch. Kaduk for performing the measurements and to M. Reuther for the support in preparing the diagrams.

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FIELD TESTS OF ELASTOL AND DEMOUSSIFIER

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ABSTRACT

The effectiveness of two oil spill treating agents were tested at sea. The agent Elastol, which imparts a viscoelastic property to oil, and a demoussifier (Brand M) were applied to ten test slicks laid midway between Nova Scotia and Sable Island. Observations of the physical characteristics of the treated slicks and chemical analysis of oil samples taken from the slicks at time intervals ranging from one to six hours indicate that both agents are at least as effective as they have been shown to be in laboratory and large-tank tests. Application of the demoussifier in concentrations ranging from 250-4000 ppm effectively prevented the formation of water-in-oil emulsions and broke up pre-existing emulsions. When applied at levels between 1000 and 9000 ppm, Elastol was found to increase the viscoelasticity of crude oil to a greater extent than was expected on the basis of results from laboratory tests. Application effects were not noted with either product. Due to weather conditions at the time of the field trials, it was not possible to determine the effect of the treating agents on the ability to recover the oil.

INTRODUCTION

To aid in the recovery of petroleum hydrocarbons spilled at sea, two chemical agents to modify the physical properties of spilled oil recently have been introduced. Elastol¹ is a proprietary formulation that comprises a high molecular weight isobutylene polymer coated with a metallic soap. These compounds are insoluble in water, but form solutions in non-polar solvents which exhibit viscoelastic behaviour. Oil slicks floating on water that have been so treated have enhanced cohesive forces and thus should be more easily contained, collected and separated from the water. Small scale laboratory tests of the effect of this material on the physical properties of oil have been undertaken by the manufacturer (Waters and Haderman 1987) as well as by Environment Canada (Bobra et al. 1987a) who have also studies these materials in a meso-scale outdoor tank test. The results of these studies show that the elasticity of various oils is indeed enhanced and that tank-confined slicks have significantly modified in their physical characteristics. Consequently, further large-scale ocean tests were recommended.

Certain types of petroleum oils are prone to form water-in-oil emulsions (mousse) which adversely affect such cleanup procedures as mopping, skimming, and pumping (National Research Council 1985). The high

¹ General Technology Applications, Inc., Manasssas, VA.

water content (30-50% and higher) also inhibits combustion. A surface active agent to break water-in-oil emulsions was also tested as a part of this project. The agent tested was Brand M, a liquid demulsifier-demoussifier, as formulated by Environment Canada. It contains a variety of polymeric agents in a hydrocarbon carrier.

MATERIALS & METHODS

Logistics

Field operations were mobilized at the Canadian Coast Guard Station at Mulgrave, Nova Scotia. The test were conducted at sea from the CCGS Mary Hichens. Ten slicks were laid near 44°15'N 61°50'W which lies about halfway between Halifax and Sable Island. This area is at least 60 km from the nearest coastline. The tests took place on Sept 9 (demoussifier) and September 10 (Elastol) 1987. The locations where the slicks were laid are shown on figure 1.

Slick laying procedure

Two petroleum mixtures were used in the field trials: 1) Alberta Sweet Crude Oil (waxes and asphaltenes removed) and 2) a mixture (50:50) of the crude oil and Bunker A (Bunker C cut with ca. 20% diesel fuel). The mixture was prepared by pumping the oils (crude oil first followed by Bunker A) into a large (23,000-liter) cylindrical tank. Volumes were determined geometrically from dipstick level measurements. The crude oil was stored in a second storage tank. Both tanks were subsequently secured to the aft deck of the Mary Hichens.

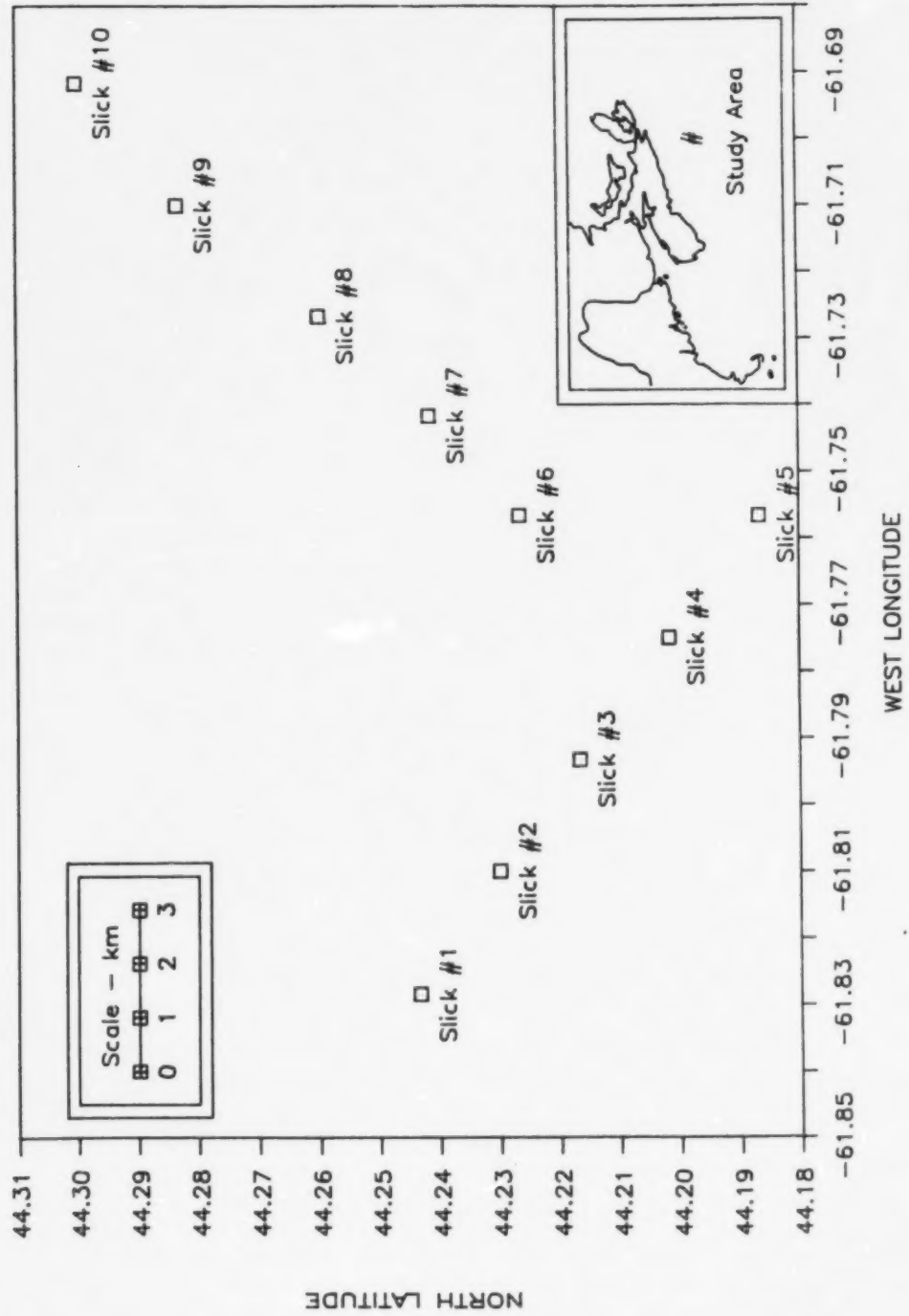
Prior to each spill, 800 liters (5 bbl) portions of oil were pumped from the large storage tanks into the spill tanks. In the case of the demoussifier trial, the spill tanks were discharged via a 2.5-inch hose equipped with flotation along its length and fitted with a paravane at the end to prevent flapping or snaking. The end of the discharge hose trailed approximately 10 meters behind the vessel while oil was being pumped. When the contents of the spill tank were completely discharged, a 2-way valve was actuated which allowed seawater to be pumped through the hose, thus flushing out the residual oil and minimizing the amount of oil trailed behind the ship as it proceeded to the next spill site. During the Elastol trials, the same plumbing arrangement was used to discharge the oil, but the end of the discharge hose was fixed near the starboard side of the ship, about 14 m ahead of the stern. This arrangement was used so that the oil could be treated as it passed by personnel on the aft deck.

Slick treatment procedure

One slick in both the demoussifier and Elastol trials was laid using oil that was treated with the appropriate agent immediately prior to discharge from the spill tank ('pre-treated' slicks). The agent was added to the spill tank concurrently with the oil being pumped from the bulk tank to ensure that the agent would be well-mixed with the oil.

All other slicks (except the control slicks) were treated after laying using specially constructed applicators. Modified Campbell-Hausefield sandblasters (Power Blast Model AT1210) were used to dispense both the demoussifier and Elastol (figure 2). The modified apparatus was designed by Environment Canada after evaluating several application systems on the basis

FIGURE 1: SLICK LOCATIONS



of their uniform distribution characteristics, portability and ruggedness, safety and simplicity. Extensive testing of the distribution pattern obtained by use of this applicator was undertaken by Bobra et al. (1987b). The applicators used for Elastol were fitted with vented hoppers to ensure continuous flow of the powdered agent. Similar modifications to the sandblasters were not required for application of the liquid demoussifier.

During the demoussifier trial, the slicks were treated immediately after they were laid (except for slick #4 whose treatment was delayed for 6 hours) from small sample boats. The procedure that was generally followed was to approach the slick from up wind and spray the slick with the agent while the sample boat traversed the slick in a zig-zag pattern until the downwind side of the slick was reached. This process was repeated until the entire dose of the treating agent had been applied.

During the Elastol trial, heavy seas prevented the use of the sample boats. As explained earlier, the oil was sprayed with the agent as it passed by personnel operating the treatment applicators on the aft deck of the vessel.

Sample collection

Samples at various time intervals were taken from the slicks with the aid of plastic mesh baskets on the end of aluminum poles. The baskets are of a type commercially available for removing debris from swimming pools; the poles were fabricated by Environment Canada. The baskets were swept half-submerged through the slicks and when a sufficient amount of oil had been collected, the plastic mesh was snipped from the frame and allowed to fall into a 5-liter pail which was then labelled and sealed. Care was taken to obtain representative samples of the slicks, i.e. samples were not taken from sheen areas or exclusively in thickly covered areas.

During the demoussifier trial, samples were collected from small sample boats. For each slick, samples were taken approximately one hour and four hours after the application of the demoussifier. In the case of slick #1, a third sample was obtained 24 hours after application. During the collection period, the samples were periodically returned to the laboratory aboard the Mary Hichens to enable prompt analyses for water content and viscosity.

Heavy weather was encountered during the day of the Elastol trial; consequently all sampling was done from the deck of the Mary Hichens. Baskets on extension poles were used to collect the samples, usually from the port side of the ship. All other sampling procedures were the same as in the demoussifier trial.

Analytical procedures

Oil samples taken from the slicks were processed as soon as possible on board the Mary Hichens where the following determinations were made: water content (spectrophotometry), viscosity (Brookfield), and elasticity (die swell).

The die swell apparatus used was similar to that described by Bobra (1987a) but used a mechanical syringe pump rather than air pressure as the driving force. The assembly comprised a plastic syringe fitted with a 12 gauge needle with the end cut at 90°. The syringe was filled with oil and a steady flow of oil established by means of the mechanical pump. The swelling of the stream of oil as it emerged from the tip of the needle was photographed with a Polaroid camera connected to a Leitz microscope.

RESULTS

Meteorological/oceanographic conditions

Meteorological observations (wind speed and direction, temperature, sea state) were taken at regular intervals by the watch keeper on the bridge of the Mary Hichens. Wave height and frequency data were collected by a waverider buoy. These data were collected to enable us to assess the effect of the wave climate on behaviour of the slicks. In particular, a high-energy climate favors the formation of water-in-oil emulsions. Waves also are a source of energy for mixing the treating agents with the oil slick.

The energy of the surface waves increased dramatically between the time the trials began on the morning of 9 Sept. and the evening of 10 Sept. The amount of wave associated energy that the slicks experienced can be estimated by the relationship,

$$E = \frac{\rho g H^2}{8} \quad (1)$$

where ρ is the density, g the acceleration of gravity, and H the wave height. It is sufficient for the purpose of comparing wave energies at different times during our experiment to allow that the energy is proportional to the square of the wave height.

As table 1 shows, the relative wave energy increased by a factor of seven during the trials. The significant wave height increased from 0.5 m to 2.5 m and breaking waves were evident throughout this period.

Table 1: Relative wave energy

Day/Time		Relative wave energy
-----		-----
09/09/87	1400	1.0
	1800	2.2
	2200	7.7
10/09/87	0400	4.7
	0800	7.0
	1600	6.7

Physico/chemical measurements demoussifier-treated slicks

The first five slicks laid using the crude/bunker mixture and were treated with the following concentrations of Brand M demoussifier:

Table 2: Demoussifier treatment concentrations

ID	Concentration of demoussifier	Comments
Slick #1	1000 ppm	Medium dose
Slick #2	250 ppm	Low dose
Slick #3	0 ppm	Control slick
Slick #4	4000 ppm	High dose (delayed treatment)
Slick #5	1000 ppm	Medium dose (pre-treated)

Oil samples were collected from the slicks approximately one hour and five hours after being treated. Table 3 and figures 3 and 4 show the results of the viscosity and water content measurements that were made on these samples on board the ship.

Table 3: Viscosity & water content of slicks 1-5

Slick #	Concentration of demoussifier	Viscosity (cp)		Water content (%)		Occurrence of mousse	
		1hr	5hr	1hr	5hr	1hr	5hr
3	0 ppm	6350	320000	88	95	++	++
2	250 ppm	2700	62250	54	93	-	-
1	1000 ppm	10000	84250	84	90	-	-
4	4000 ppm	2200	105000	72	90	+	+\$
			22600		78		-†
5	1000 ppm*	970	38500	32	80	-	-

* pretreated; \$ at 6 hours - before treatment; † after treatment

The demoussifier was very effective in preventing large viscosity increases in the treated slicks. The samples taken from the slicks one hour after being treated showed relatively uniform viscosities in the range of 2000 to 10000 cp, with the pretreated slick having the lowest viscosity. The samples taken approximately five hours after treatment all had higher viscosities. The control slick exhibited the highest viscosity and a heavy mousse was prevalent. However, the slicks treated with the low and medium doses of demoussifier had dramatically lower viscosities than the untreated slick and no evidence of mousse was noted in either case.

The untreated slick #4 had a high viscosity and developed patches of mousse at the 5 hour time interval. When this slick was treated with demoussifier, the mousse began to break up and the viscosity measured one hour after treatment had fallen to 20% of the pretreatment level. The mousse broke up almost immediately in areas that were directly sprayed. The emulsion broke up over a period of minutes in other areas of the slick, where presumably the demoussifier flowed in from sprayed areas.

As figure 4 indicates, water content is not a good indicator of mousse formation; all slicks accumulated a large amount of water. While, some formed mousse as evidence by the reddish colouration, high viscosity and

FIGURE 3: VISCOSITY OF SLICKS 1-5

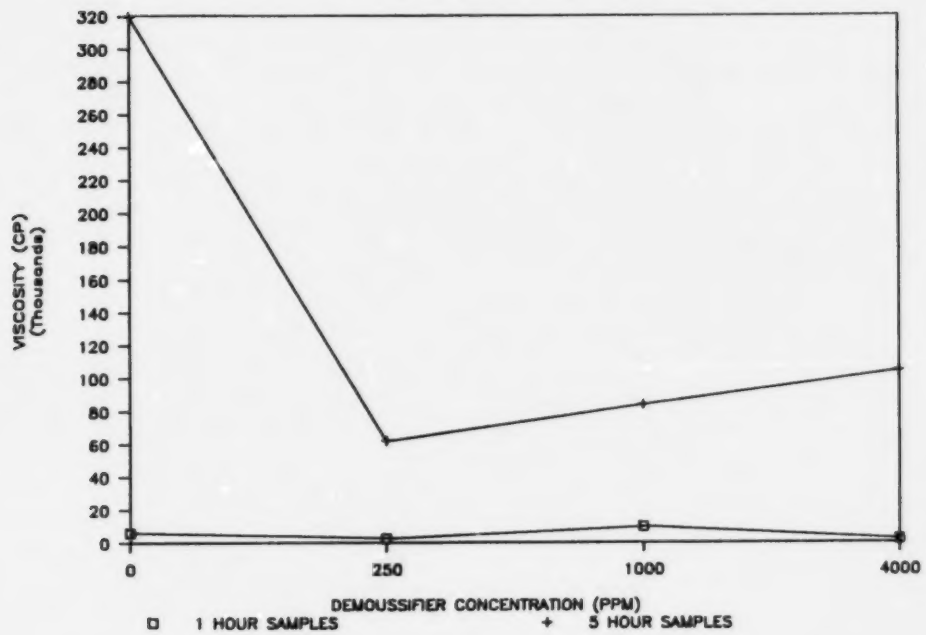
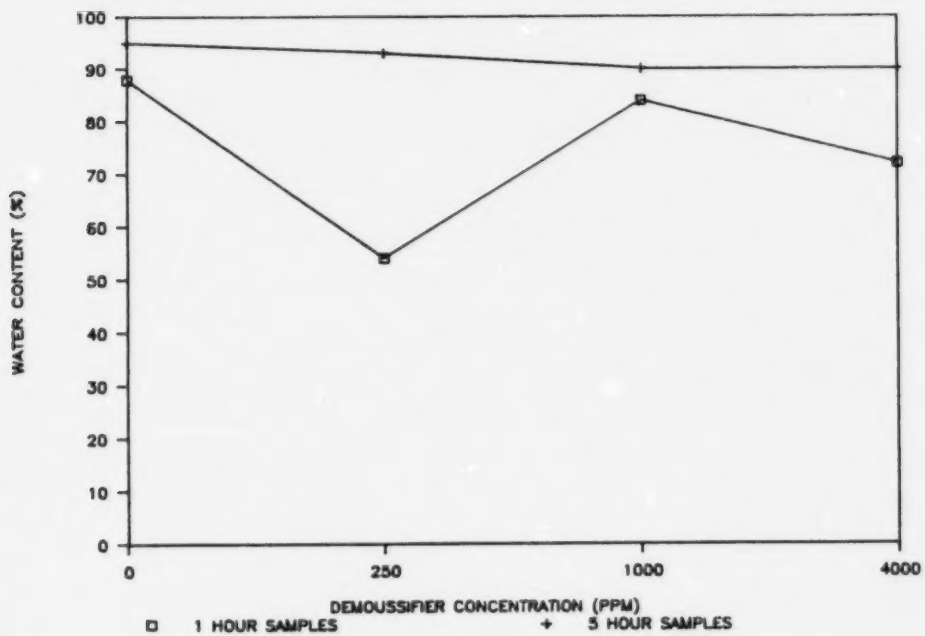


FIGURE 4: WATER CONTENT OF SLICKS 1-5



stability, others did not but still had high water contents. Current models do not predict the high water contents observed during this field trial.

To summarize, the demoussifier appeared to work very well. The slicks treated with demoussifier at the time of laying and the pretreated slick had markedly lower viscosities and showed no tendency to form mousse while the untreated slicks became heavily moussified. Demoussifier applied to a slick that had already developed mousse had the effect of rapidly breaking up the emulsion.

Physico/chemical measurements Elastol-treated slicks

The five crude oil slicks laid during the Elastol trials were treated with the following concentrations of the agent:

Table 4: Elastol treatment concentrations

ID	Concentration of Elastol	Comments
Slick # 6	3000 ppm	Medium dose
Slick # 7	1000 ppm	Low dose
Slick # 8	0 ppm	Control slick
Slick # 9	9000 ppm	High dose (delayed treatment)
Slick #10	3000 ppm	Medium dose (pre-treated)

Oil samples were collected from the slicks approximately one hour and five hours after being treated. Table 5 and figures 5 and 6 show the results of the viscosity and elasticity (die swell) measurements that were made on these samples on board the ship.

Table 5: Viscosity & elasticity of slicks 6-10

Slick #	Concentration of Elastol	Viscosity (cp)		Elasticity (die swell)		"Observed" elasticity	
		1hr	5hr	1hr	5hr	1hr	5hr
8	0 ppm	187000	242000	0.99	0.99	none	none
7	1000 ppm	32250	228000	1.28	1.33	low	med
6	3000 ppm	29300	300000	1.33	1.35	med	high
9	9000 ppm	93000	696000	1.99	2.63	high	super
10	3000 ppm*	170500	156000	1.35	1.57	med	high

* pre-treated

The viscosity and die-swell measurements made on the oil samples taken from the slicks as well as observations of the physical properties of the slicks taken at sampling time all indicate that Elastol was effective in

FIGURE 5: VISCOSITY OF SLICKS 6-10

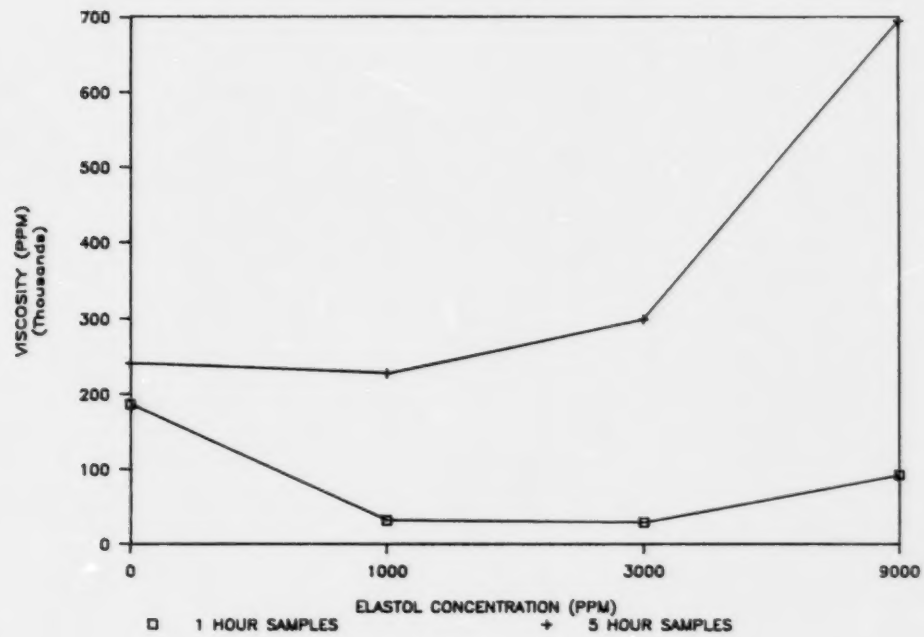
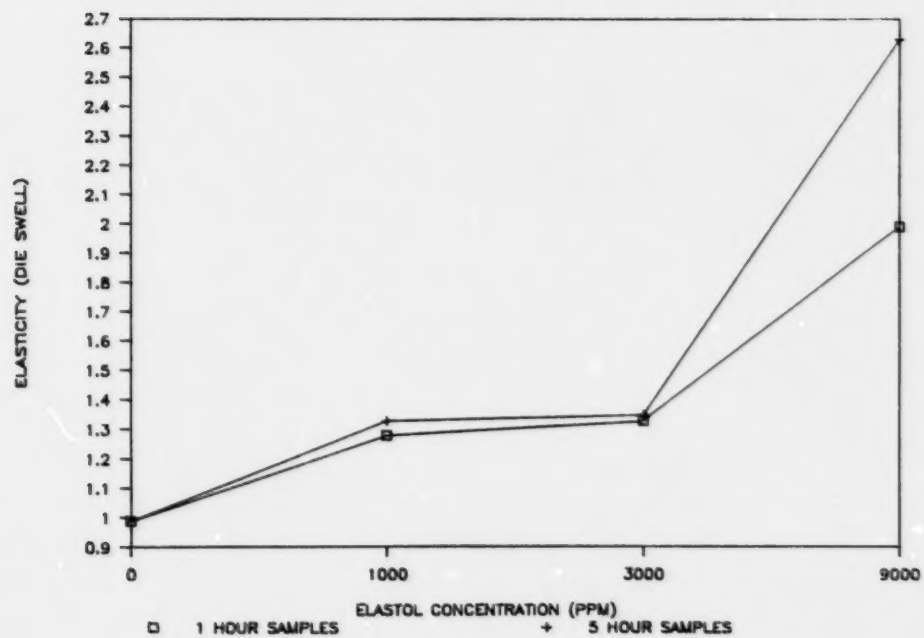


FIGURE 6: ELASTICITY OF SLICKS 6-10



increasing the viscoelasticity of the oil. As shown in table 5 and figure 5, the viscosity of the Elastol-treated slicks increased 7.5-10 fold over a five hour period. The untreated slick, though having a high viscosity at the one-hour interval, increased by only 20% over the same interval, presumably as a result of uptake of water and/or emulsion formation (Bobra 1987a). The growth of viscosity in the treated slicks, on the other hand, shows a clear relationship to the concentration of Elastol applied (figure 5).

The die swell measurements show more distinctly the effects of the treatment on the visco-elasticity of the oil. Samples taken from the control slick at one and five hours had die-swell ratios of unity (no elasticity) while those from the slicks treated with low and medium concentrations of Elastol had ratios of about 1.35. These ratios are as high or higher than the results obtained by Bobra (1987a) from laboratory tank tests in which similar concentrations of Elastol were used. It is also interesting to note that the maximum die swell ratios were reached before the one-hour sampling time and remained essentially unchanged at the five-hour sampling time.

The slick treated with the highest dose (9000 ppm) of Elastol showed the highest elasticity with the die swell ratio increasing from 2 to 2.6 over the five-hour interval between samples. While all of the samples taken from the treated slicks were obviously elastic at sampling time, the five-hour sample collected from the slick treated with 9000 ppm Elastol appeared to be almost semi-solid (super-elastic - table 5). This slick showed a higher elasticity than any of the samples from the laboratory tests of Elastol (Bobra 1987a), presumably as a result of the high mixing energy prevalent at the time of the field trials.

In summary, Elastol worked as well or better than expected under the conditions of an actual spill. High elasticities were observed at all treatment concentrations.

CONCLUSIONS

The period over which the trials were run was characterized by high wave energy and this tended to disperse the test slicks only a relatively short time (ca. 12 hours) after they were laid. Thus the long-term effects of the treating agents can not be assessed from the data collected during this study. However, the following observations were made on the physical behaviour of the slicks over a four to six hour period after the treatment agents were applied:

- Brand M demoussifier worked well. The formation of water-in-oil emulsions was inhibited in the slicks treated with demoussifier.
- The direct application of the demulsifier to patches of mousse in the untreated slicks had the immediate effect of breaking up the emulsion (10-15 seconds).
- Mousse in areas of the slick not directly sprayed appeared to break up when the agent migrated from sprayed areas (ca. 10 minutes).

- Water content did not appear to be a good indicator of mousse formation; all slicks accumulated a large quantity of water whether mousse was present or not.
- Elastol increased the viscoelasticity of the oil in the treated slicks to a greater extent than expected from previous laboratory studies.
- The manner in which either of the agents was applied did not seem to particularly critical, i.e. if the agents were applied in a non-uniform manner, they appeared to migrate to all portions of the slick through the mixing action of the waves.

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DISPERSANT EFFECTIVENESS AT SEA: A HYPOTHESIS TO EXPLAIN
CURRENT PROBLEMS WITH EFFECTIVENESS

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Introduction

Dispersants have been a controversial issue since the time of the TORREY CANYON incident. The concern, until recently, has been with the toxicity and environmental effects of the dispersants and the dispersed oil. In recent times, more concern has been focussed on the effectiveness of the dispersants at sea. This concern largely began in the early eighties when a large number of field trials were conducted and less than satisfactory results were obtained in most of these. A review of such trials was published in 1985 by Nichols and Parker and began the current interest in dispersant effectiveness.¹ The review listed over 35 experimental spills and noted the effectiveness assigned for the slicks. These average around 30% or 20% depending on how one takes the average. These low values were disconcerting to many people, since removal of that little oil would not constitute a great benefit in many cleanups.

This author reviewed field experimental spills in a number of recent papers, the last of which listed 106 experimental spills.^{21,22} Table 1 summarizes the review of these experimental spills. The spills have been conducted over the past 12 years and are all spills of more than one barrel. Of the 106 spills, 23 were controls used to establish a comparison. Percentage effectiveness is computed for 25 spills, all of them in the earlier group. Effectiveness values range from 2 to 100% and average 33%. The present author has analyzed these effectiveness measures and has concluded that values reported here are high and are all made on the basis of water column mass balance measurements. These in turn, are based on the assumptions that a regular distribution of oil exists in the water column, that the oil in the water column is spatially related to the surface slick, that oil in the water column does not resurface and that a simple integration scheme can sum oil in the water column. The paper showed that none of these assumptions are true, and that mass balance measurements are tentative at best and will lead to overestimation of effectiveness.

In addition, a number of phenomena interfere with effectiveness observations, both in field trails and during actual usage; they are herding, resurfacing of the oil and formation of emulsion particles.²¹

At best it can be said that at this time the effectiveness of dispersants in the field is questionable. This paper will put forward a hypothesis directed at explaining this observation and will also offer some solutions.

TABLE 1 -- Data from dispersant effectiveness trials

Location/ Identifier	Reference	Year	Number	Oil Type	Spill Amount (m ³)	Dispersant	Application Method	Dose Rate	Sea State	Claimed Effectiveness	
										(%)	(%)
North Sea	Cormack and Nichols (1,2)	1976	1	Ekofisk	0.5	10% Conc.	Ship, WSL	-	1	-	-
			2	Kuwait	-	10% Conc.	Ship, WSL	1:20	2-3	100	100
Wallops Island	McAuliffe et al (1,3)	1978	3	Murban	1.7	Corexit 9527	Helicopter	1:5	1	-	-
			4	La Rosa	1.7	Corexit 9527	Helicopter	1:5	1	-	-
			5	Murban	1.7	Corexit 9527	Helicopter	1:11	1	100	100
			6	La Rosa	1.7	Corexit 9527	Helicopter	1:11	1	50	456
South California	Smith et al (4)	1978	7	North Slope	1.7	Control later Corexit 9527	Control then Helicopter	1:5	0-1	-	-
			8	North Slope	3.2	Corexit 9527	Airplane, Cessna	1:5	0-1	-	-
			9	North Slope	1.7	Recovery + Corexit 9527	Helicopter	1:5	0-1	-	-
			10	North Slope	0.8	BP1100WD	Ship, WSL	1:5	0-1	-	-
			11	North Slope	0.8	Corexit 9527	Ship	1:5	0-1	-	-

TABLE 1 (.../continued)

<u>Location/ Identifier</u>	<u>Reference</u>	<u>Year</u>	<u>Number</u>	<u>Oil Type</u>	<u>Spill Amount (m³)</u>	<u>Dispersant</u>	<u>Application Method</u>	<u>Dose Rate</u>	<u>Sea State</u>	<u>Claimed Effectiveness (%)</u>
South California	Smith et al (4)	1978	12	North Slope	3.2	Corexit 9527	Airplane, Cessna	1:5	1-2	-
			13	North Slope	0.8	Corexit 9527	Ship	1:5	1-2	-
			14	North Slope	0.8	BP1100WD	Ship, WSL	1:5	1-2	-
			15	North Slope	0.6	Several, Demonstration	Several, Demonstration	-	1-2	-
Victoria	Green et al (1,6)	1978	16	North Slope	0.2	10%, 9527	Ship, WSL	1:1	2	-
			17	North Slope	0.4	10%, 9527	Ship, WSL	1:1	1	-
			18	North Slope	0.2	10%, 9527	Ship, WSL	1:1	1	-
Long Beach	McAuliffe et al (1,5)	1979	19	Prudhoe Bay	1.6	Control	Control	-	2-3	0.5
			20	Prudhoe Bay	1.6	2% Conc.	Ship	1:67	2-3	8
			21	Prudhoe Bay	1.6	2% Conc.	Ship	1:67	2-3	5
			22	Prudhoe Bay	3.2	Conc.	Airplane, DC-4	1:20	2-3	78

TABLE 1 (.../continued)

<u>Location/ Identifier</u>	<u>Reference</u>	<u>Year</u>	<u>Number</u>	<u>Oil Type</u>	<u>Spill Amount (m³)</u>	<u>Dispersant</u>	<u>Application Method</u>	<u>Dose Rate</u>	<u>Sea State</u>	<u>Claimed Effectiveness (%)</u>
								0:0		
Long Beach	McAuliffe et al (1,5)	1979	23	Prudhoe Bay	1.6	Conc.	Airplane, DC-4	1:25	2-3	45
			24	Prudhoe Bay	1.6	Control	Control	-	2-3	1
			25	Prudhoe Bay	3.2	Conc.	Airplane, DC-4	1:27	2-3	60
			26	Prudhoe Bay	1.6	2%	Ship	1:11	2-3	11
			27	Prudhoe Bay	1.6	2%	Ship	1:11	2-3	62
Mediterranean, Protecmar I	Bocard et al (7)	1979	28-41	Light Fuel	3 each	BP1100X BP1100WD Finasol OSR-5 Corexit 9527	Ship, Helicopter, various and Airplane CL215	-	1-3	458
Mediterranean, Protecmar II		1980	42-49	Light Fuel	1-5.5	"	"	-	1-3	-
Mediterranean, Protecmar III	Bocard and Gatellier (1,7,8)	1981	50	Light Fuel	6.5	Dispolene 325	Airplane, CL215	1:3	1-2	50
			51	Light Fuel	6.5	Shell	Airplane, CL215	1:3	2-3	-
			52	Light Fuel	6.5	Control	Control	-	1-2	-
			53	ASMB	2.5	Control	Control	-	1	-
Newfoundland	Gill et al (9)	1981	54	ASMB	2.5	Corexit 9527	Airplane, DC-6	1:10	1	-

TABLE 1 (.../continued)

Location/ Identifier	Reference	Year	Number	Oil Type	Spill Amount (m ³)	Dispersant	Application Method	Dose Rate	Sea State	Claimed Effectiveness (%)
Norway	Lichtenthaler and Daling (1,10)	1982	55	Statfjord	0.2	Control	Control	-	2-3	0.6
			56	Statfjord	0.2	10% Conc.	Ship	1:10	2-3	6
			57	Statfjord	0.2	10% Conc.	Ship	1:10	2-3	17
			58	Statfjord	0.2	Control	Control	-	2-3	2.6
			59	Statfjord	0.2	10% Conc.	Ship	1:17	2-3	19
			60	Statfjord	0.2	10% Conc.	Ship	1:18	2-3	22
			61	Statfjord	0.2	10% Conc.	Ship	1:13	2-3	2
North Sea	Cormack (1,11)	1982	62	Arabian	20	Control	Control	-	1	-
			63	Arabian	20	Corexit 9527	Airplane, Islander	1:2	1	-
			64	Arabian	20	Corexit 9527	Airplane, Islander	1:4	1	-
			65	Light Fuel	3	10% Dispolene 325	Ship	1:2	3	-
Mediterranean Protecmar V	Bocard et al (1,12)	1982	66	Light Fuel	5	Dispolene 325	Airplane, CL215	1:2.4	3	-

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TABLE 1 (.../continued)

<u>Location/ Identifier</u>	<u>Reference</u>	<u>Year</u>	<u>Number</u>	<u>Oil Type</u>	<u>Spill Amount</u> (m ³)	<u>Dispersant</u>	<u>Application Method</u>	<u>Dose Rate</u>	<u>Sea State</u>	<u>Claimed Effectiveness</u> (%)
Protecmar V	Bocard et al (1,12)	1982						0:0		
			67	Light Fuel	5	Dispolene 325	Ship	1:2.8	2	-
			68	Light Fuel	5	Dispolene 325	Airplane, CL215	1:2.8	2	-
			69	Light Fuel	3.5	Dispolene 325	Ship	1:2.6	1-2	-
			70	Light Fuel	4	Dispolene 325	Helicopter	1:2.9	1-2	-
Holland	Delvigne (1,13)	1983	71	Light Fuel	2	Premixed	Premixed	1:20	1-2	40-50
			72	Light Fuel	5	Control	Control	-	2	460
			73	Statfjord	2	Control	Control	-	1-2	2
			74	Light Fuel	2	Control	Control	-	1-2	2
			75	Statfjord	2	Control	Control	-	1	2
			76	Statfjord	2	Finasol OSR-5	Airplane	1:10-30	1	2
			77	Light Fuel	2	Finasol OSR-5	Airplane	1:10-30	1	2
			78	Statfjord	2	Finasol OSR-5	Premixed	1:20	2-3	100

TABLE 1 (.../continued)

Location/ Identifier	Reference	Year	Number	Oil Type	Spill Amount (m ³)	Dispersant	Application Method	Dose Rate	Sea State	Claimed Effectiveness (%)
Holland	Delvigne (1,13)	1983	79	Light Fuel	2	Control	Control	-	2-3	2
			80	Statfjord	2	Finasol OSR-5	Airplane	1:10-30	1-2	2
			81	Statfjord	2	Finasol OSR-5	Airplane	1:10-30	1-2	2
Halifax	Swiss and Gill (1,14,15)	1983	82	ASMB	2.5	Corexit 9527	Helicopter	1:20	1	2.5
			83	ASMB	2.5	Control	Control	-	1	1
			84	ASMB	2.5	Corexit 9550	Helicopter	1:10	1	13
			85	ASMB	2.5	Control	Control	-	1	1
Norway	Lichtenthaler and Daling (16)	1984	86	ASMB	2.5	BP MA700	Helicopter	1:10	2-3	10-41
			87	ASMB	2.5	Control	Control	-	2-3	7
			88	Statfjord	10	Control	Control	-	1	-
			89	Statfjord	10	Corexit 9527	Airplane, Islander	1:75	1	-
			90	Statfjord	10	Control	Control	-	2	-

TABLE 1 (.../continued)

<u>Location/ Identifier</u>	<u>Reference</u>	<u>Year</u>	<u>Number</u>	<u>Oil Type</u>	<u>Spill Amount (m³)</u>	<u>Dispersant</u>	<u>Application Method</u>	<u>Dose Rate</u>	<u>Sea State</u>	<u>Claimed Effectiveness (%)</u>
Norway	Lichtenthaler and Daling (16)	1984	91	Statfjord	10	Corexit 9527	Airplane	1:80	2	-
Brest, Protecmar VI	Bocard (7,17)	1985	92	Statfjord	12	Corexit 9527	Premixed	1:33	2	-
			93	Statfjord	10	Corexit 9527	Airplane	1:50	-	-
			94	Fuel Oil	5	Control	Control	-	1	-
			95	Fuel Oil	28	Dispolene 355	Helicopter	1:9	1	-
			96	Fuel Oil	part of above	Dispolene 355	Ship-spray	1:9	1	-
Haltenbanken	Sørstrøm (19)	1985	97	Fuel Oil	part of above	Dispolene 355	Ship-aerosol	1:9	1	-
			98	Topped Statfjord Crude	12.5	Control	-	-	1-2	-
			99	Topped Statfjord Crude	12.5	Finasol	Premixed, Injected 3 m below surface	1:50	1-2	-

TABLE 1 (.../continued)

Location/ Identifier	Reference	Year	Number	Oil Type	Spill Amount (m ³)	Dispersant	Application Method	Dose Rate	Sea State	Claimed Effectiveness (%)
Haltenbanken	Sørstrøm (19)	1985	100	Topped Statfjord Crude	12.5	Control	-	-	1-2	-
			101	Topped Statfjord Crude	12.5	Alcopol (demulsifier)	Premixed	250 ppm	1-2	-
Beaufort Sea	Swiss et al (20)	1986	101 (CA)	Topped Federated Crude	2.5	Control	-	-	1-2	-
			102 (CB)	Topped Federated Crude	2.5	Control	-	-	1-2	-
			103 (C1)	Topped Federated Crude	2.5	BP MA700	Helicopter	1:10	2-3	-
			104 (T1)	Topped Federated Crude	2.5	BP MA700	Helicopter	1:1	2-3	-
			105 (T2)	Topped Federated Crude	2.5	Corexit CRX-8	Helicopter	1:1	2-3	-
			106 (C)	Topped Federated Crude	2.5	Control	-	-	2-3	-

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Abbreviations: ASMB - Alberta Sweet Mixed Blend; Conc. - Concentrate; WSL - Warren Springs Laboratory

Surfactants

Figure 1 shows a variety of surfactant types that have been used in oil spill control over the past 20 years. A surfactant consists of a molecule with a oil-soluble portion (oleophilic or lipophilic) and a water-soluble portion (hydrophilic). A surfactant functions by bridging the gap between water and oil. A surfactant with a long hydrophilic chain will allow the dissolution of oil droplets into water and one with a short hydrophilic chain will allow the dissolution of water in oil.²³

The ratio of the hydrophilic to lipophilic portion is most often described by the 'HLB' value. This stands for hydrophilic-lipophilic balance. The most common scale for HLB is one based on a range of values from 0 to 20. This scale is illustrated in Figure 2. This arbitrary assignment has meant that 1 is a strong water-in-oil emulsifier, 10 is a good disperser and 20 is a strong oil-in-water emulsifier. Caution must be exercised when using HLB values, because they are arbitrary and are calculated on the basis of the ratio of chain lengths for the hydrophilic and lipophilic portions. There is no direct way of measuring HLB, and the effect of other groups (those that are strictly not oleophilic or hydrophilic) on the surfactant molecule behaviour is known to be fairly important.

The author has tested over a hundred surfactants in the laboratory and has found that surfactants with HLB of 1 to 5 are strong water-in-oil emulsifiers, those of 6 to 12 are good dispersers and those from 12 to 20 are highly water soluble and have little use in dispersants. Amongst all of these surfactants there were those which did not behave at all like their HLB indicates. For example, one surfactant with an HLB of 10.2 caused the formation of a water-in-oil emulsion in a standard laboratory test. Most other surfactants did not do so unless their HLB's were less than 6.

There is also a certain amount of sensitivity to HLB. In laboratory testing a family of surfactants, it was found that one member had no dispersing action at an HLB of 10.0 and its 10.2 homologue had very high dispersing action. The significance of this discussion of HLB is that, despite its importance as an indicator of what a surfactant will do, it is not entirely reliable.

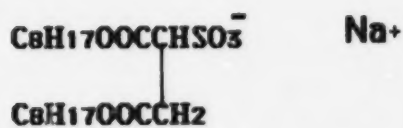
Commercial dispersant mixtures use surfactants with an average HLB value of around 10, although this has not generally been a criterion for formulation. Historically, the measured effectiveness has been used. Figure 4 shows the effectiveness of a number of surfactants and surfactant mixtures versus HLB. The figure clearly shows that overall effectiveness is highest at an HLB of 10, and that individual effectiveness of a surfactant is variable with respect to HLB. The simplest explanation of the correlation of HLB and effectiveness is that surfactants with a low HLB have a strong tendency to produce water-in-oil emulsions and this process competes with dispersion. At HLB's far above 10, the surfactant is very hydrophilic and simply leaves the oil to enter the water. This process becomes increasingly more evident as HLB increases.

Figure 1 Some Typical Surfactants

Ionic Surfactants

1. Anionic

eg. sodium dioctylsulphosuccinate



2. Cationic

not important for dispersants

3. Zwitterionic

not important for dispersants

Non-Ionic Surfactants

many subclasses based on structure

eg. fatty acid esters of anhydrous sorbitols

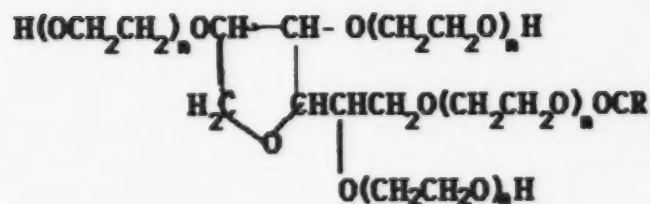
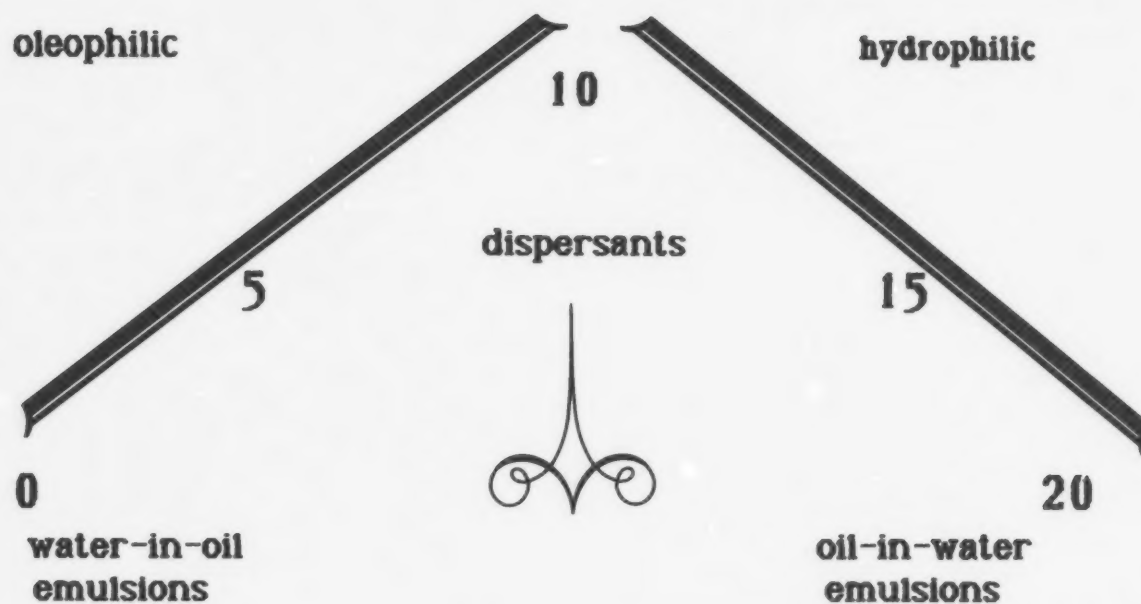


Figure 2 The HLB Scale

hyper-scale

20 to 50

- ionic surfactants
- very hydrophilic oil-in-water emulsifiers

The standard HLB scale of 1 to 20 was designed for non-ionic surfactants. Ionic surfactants generally do not fit on the scale and range between 25 and 40 on an extended scale relative to the non-ionic surfactants. Most ionic surfactants are very hydrophilic and oleophobic and are intended to work from the water to the soil. Most soaps, detergents, shampoos, etc. are examples of ionic surfactant use and application. An examination of Figure 3 and the sharp drop-off of effectiveness at higher HLB's, even as low as 15, shows that there is no hope of oil dispersion with ionic surfactants with HLB's of up to 40. Ironically, some products are marketed with only ionic surfactants. In Canada, none of the products on the standard list of accepted dispersants have large amounts of ionic surfactants.

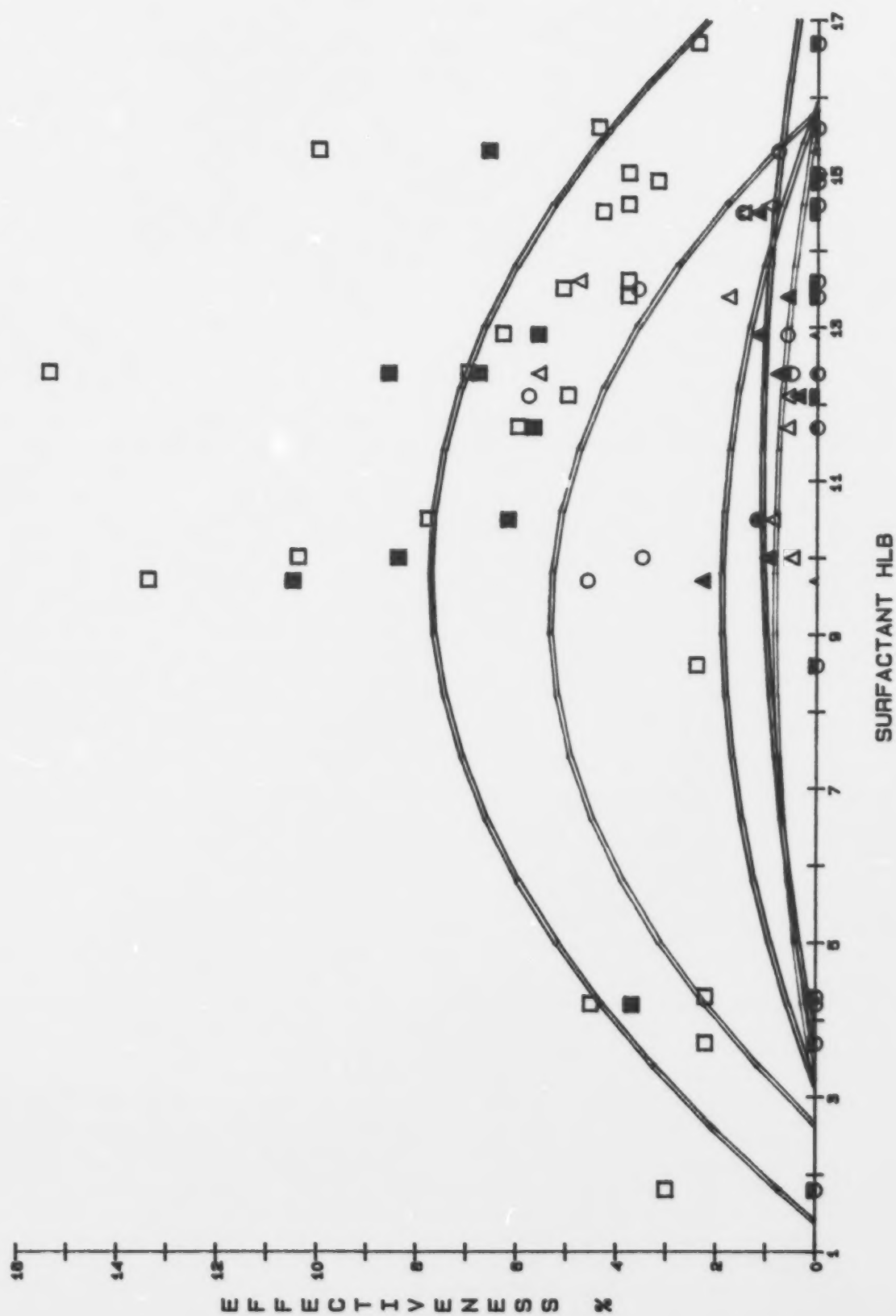
Dispersants approved in Canada are of two types with respect to their surfactant compositions; those containing one or two surfactants with HLB's very close to 10 or those containing surfactants whose average is close to 10. Dispersants which contain Tween 20 (HLB = 15) and Span 20 (HLB = 5) in equimolar portions and which have an average HLB of 10 are very common. Often an ionic surfactant is added to "improve" the effectiveness. Lab testing had shown that such products have high effectiveness and the theory was developed that this was due to the close packing of surfactant molecules at the oil-water interface, because ionic surfactants have small hydrophilic portions and these could pack tightly with the large non-ionic hydrophilic portions. It will be demonstrated later that both this idea and the idea of mixing widely different HLB's pose problems. The surfactant mixture is always in a solvent which helps the product application and mixing with the oil after application. The solvent systems could also be described as being of two types, oil-based or water-soluble solvent based. The oil-based solvents are generally high-boiling naphtha solvents similar to paint thinners. The water-soluble solvents include glycols, cellusolves and polyols. Water-soluble solvents were used to provide dispersants that could be diluted with water.

The Dispersion Process

Recently, sophisticated techniques and equipment have enabled researchers to study what the dispersion mechanisms are and what particle sizes are produced. Equipment includes x-ray diffraction, laser and optical particle counters and epifluorescent microscopes.^{24,25} Although knowledge is far from complete, it does enable us to understand basic concepts and why dispersants function the way they do.

A very important concept in understanding surfactants in any concept or usage is the understanding of 'micelles'. These are aggregates of surfactant molecules in a medium such as water. Such aggregations may occur in oil but neither their existence nor even the theoretical potential for their existence is established. Micelles in water consist of surfactant molecules lined up with their hydrophilic portions in the water and their oleophilic portions together. This is the most stable way for large amounts of surfactant to exist in water. Once the

Figure 3
THE ROLE OF HLB ON EFFECTIVENESS



surfactant concentration in water rises to a certain level, known as the CMC or the critical micelle concentration, additional surfactant in the water simply ends up forming micelles. Micelle formation affects oil dispersion in two ways, first it is a competing mechanism and 'consumes' surfactant molecules. Secondly, micelles can solvate oil components inside the oleophilic area. Such oil is relatively stable when dissolved in this manner since micelles are relatively stable themselves and are neutrally buoyant. Micelles are small, ranging in size from 100 to 5000 Angstroms (.0001 to .005 microns) and are not optically visible with even the most powerful microscope. Electron microscopes and x-ray diffraction techniques must be used to study micelles. An intermediate class of particles, known as swollen micelles, consist of micelles with large amounts of oil in the centre. Their size ranges from .05 to .1 microns. These particles are not well-studied and are not thought to be important to oil dispersion.

Oil dispersion largely takes place as emulsification, consisting of oil droplets with surfactant molecules lined up at the interface. There are three generic classes of emulsions. The smallest or micro-emulsions range in particle size of 0.1 to 1 microns. The term micro-emulsion is also used to describe emulsions of water-in-oil with small particle sizes. Little is known about micro-emulsions as contributors to oil dispersion. Studies show that few particles of this size range are created. The most important particle size range formed in dispersion is that of the 1 to 50 microns, the range in which most of the oil-in-water dispersions are found. Particles greater than this size, eg. macroemulsions, are not stable and rapidly rise to the surface if driven into the water.

Studies have shown that the most frequent particle size formed from either natural or chemical dispersion is about 10 microns. The difference between chemical and natural dispersion is not the particle size but the greater number of small particles.^{26,27} Only highly energetic systems will keep a particle of greater than 100 microns in the water column.

Laboratory Testing

Expectations for field effectiveness values are largely derived from laboratory testing, particularly values from the Labofina and the MNS (Mackay-Nadeau-Steelman) or Mackay test. The latter test in particular yields very high results. Recent review of test results has shown that the values from the Mackay test are unrealistically high because of the high energy input to the system, the lack of settling time in the protocol and the fact that the sampling point happens to be at a location in the apparatus where most droplets collect.^{28,29} A new test, known as the swirling flask test, produces results which are believed to be more realistic. Table 2 shows some swirling flask results for various oils and three dispersants. These values were obtained having dispersant premixed in the oil at a ratio of 1:25 (dispersant:oil). For this paper, the results from a highly dispersible oil, Alberta Sweet Mixed Blend (ASMB), will be used as

the basis for further discussion. Table 2 shows that dispersability for ASMB varies between about 30 and 60 %. This is at the top end of dispersion in a laboratory setting. Thirty percent dispersion may not yield enough practical benefit to warrant the use of dispersants in some situations. In fact, as will be demonstrated later, field effectiveness can be much lower.

Dispersant Effectiveness in The Field

A number of physical/chemical processes intervene in field situations to bring effectiveness values below those measured in the laboratory. Some of these have been described in the literature.³⁰ Three new and major sources of losses have been found. These are:

1. separation of surfactants in dispersant mixtures and sloughing-off of the hydrophilic portions directly into the water column,
2. direct loss of surfactant to the water column from the water surface, and
3. loss of surfactant from emulsion droplets in the water column.

As noted earlier, a number of manufacturers mix surfactants of various HLB's to yield an overall value of about 10. Until recently this was generally accepted as the way to obtain better overall performance because of the more stable emulsions resulting from the close-packing achievable with different size surfactants. A number of researchers have recently found that such mixtures separate into hydrophilic and oleophilic components when applied to a oil/water interface.³¹ The present author has also seen evidence of this in the laboratory. If such separation occurs, there should be some evidence of it at field trial applications. Indeed, recent analysis of multi-spectral data from the 1986 Beaufort Sea trial reveals that sloughing-off of a material is very evident in the blue-green region of the spectrum, and it only appears on treated slicks. A sparkling region in the blue-green appears on each of the treated slicks near the region of highest treatment and this region gradually separates from the main slick and then disappears in about 1/2 hour. It is hypothesized that this is surfactant separation and that the surfactant slowly becomes mixed with the water and disappears. Its differential movement is explained by the fact that it is in a different current regime than the surface slick.

The second new "loss" phenomenon is dispersant movement into the water column directly from the water surface. It has been found in the laboratory that dispersant contacting water directly will largely be lost to the water and the remaining portion will only disperse oil to a limited extent. Additionally it has been noted that dispersant droplets can move through the oil layer and directly contact the water without significant mixing in the oil. A dramatic loss in effectiveness is illustrated in Table 3, where values for pre-mixed versus dropwise application are shown. Each result is an average of at least two runs and the values are repeatable within 5%.

TABLE 2 -- Dispersant effectiveness using the swirling flask apparatus

<u>Oil Type</u>	<u>Effectiveness (%)</u>		
	<u>Dispersant</u>		
	<u>Corexit 9527</u>	<u>Enersperse 700</u>	<u>CRX-8</u>
Alberta Sweet Mixed Blend	30	48	37
Amauligak	48	54	56
Atkinson	7	8	9
Avalon (19.8% evaporated)	8	13	10
Federated	39	38	23
Gear oil	29	10	40
Hibernia (11.7% evaporated)	11	6	12
Issungnak	24	42	42
Kuwait	5	7	4
Lago Medio (19.9% evaporated)	0	2	7
Norman Wells (12% evaporated)	23	31	37
Prudhoe Bay	7	17	5
Tarsiut	53	63	52
Uvilik	52	64	11

Table 3 The Change in Effectiveness with Application

Surfactant Designation	Percentage Dispersion	
	Pre-mixed oil/dispersant	Applied dropwise
BA	39	4
BB	29	7
BE	28	7
BF	63	4
BH	45	5
BI	44	6
BJ	53	7
BK	34	3
BL	50	8
BM	26	8
BP	59	42
BQ	98	34
BS	60	14
BT	34	25
BU	56	29
BV	6	13

The third new "loss" phenomenon is that of surfactant loss from "stable" emulsion. As with most things in chemistry, the formation of emulsion is a result of thermodynamic equilibrium; the surfactant molecules both enter and leave an emulsion. In fact, in certain types of emulsions, these rates have been measured. For example, one investigator measured the surfactant entry rate as 10^3 molecules per second and the departure rate as 10^3 molecules per second.²⁴ This rate differential implies a very stable emulsion because loss of surfactant is much less than surfactant entry. This stability is true in a closed system, however when emulsion is in open systems, there is little or no surfactant available to reenter an emulsion droplet. It follows that any surfactant exchange is really surfactant loss. Over the longer term, much of the emulsion becomes destabilized by this surfactant loss and the oil droplets rise to the surface unless the water is highly turbulent and keeps droplets mechanically suspended. Figure 4 shows the effect of both droplet rising and surfactant loss as measured in a laboratory using a swirling flask apparatus. After applying energy for the usual period of 20 minutes, the oil and water were left undisturbed for long periods of time and then oil content of the water column measured at intervals ranging up to 48 hours. This Figure also shows that effectiveness varies with the type of surfactant and that effectiveness decline is not consistent. In fact, the more oleophilic products (lower HLB) show a lesser decline in effectiveness.

The effect of all these losses and other physical processes on dispersant field effectiveness is summarized in Figure 5. After the dispersant is sprayed, physical losses of dispersant reduce maximum effectiveness from 30 to 60% down to 20 to 50%. If herding occurs, much of the dispersant is lost to open water and effectiveness is reduced to very low values. If herding does not occur when the dispersant hits the oil, separation of the surfactant occurs and the hydrophilic components are lost to the water. This is estimated to cause a 50% reduction in effectiveness, this being the value derived from laboratory experiments. Additionally, there are effects of poor mixing and direct loss of surfactant from the water interface into the water column. These are estimated to reduce the maximum effectiveness to 5 to 15%. More surfactant is lost from the emulsified droplets after dispersion of the oil occurs. The large (macro-emulsion) particles will resurface in a matter of minutes and the mid-size particles in hours. This leaves a maximum of 2 to 8% dispersed oil in the water column.

Improvements to Effectiveness

The Environmental Emergencies Technology Division has conducted research over the past two years to assess whether or not dispersant effectiveness can be improved. Limited success at the laboratory scale has indicated that some improvement is possible.

Three areas in particular can be addressed:

1. loss associated with herding - laboratory work indicates that herding may be a function of the hydrophilic content.

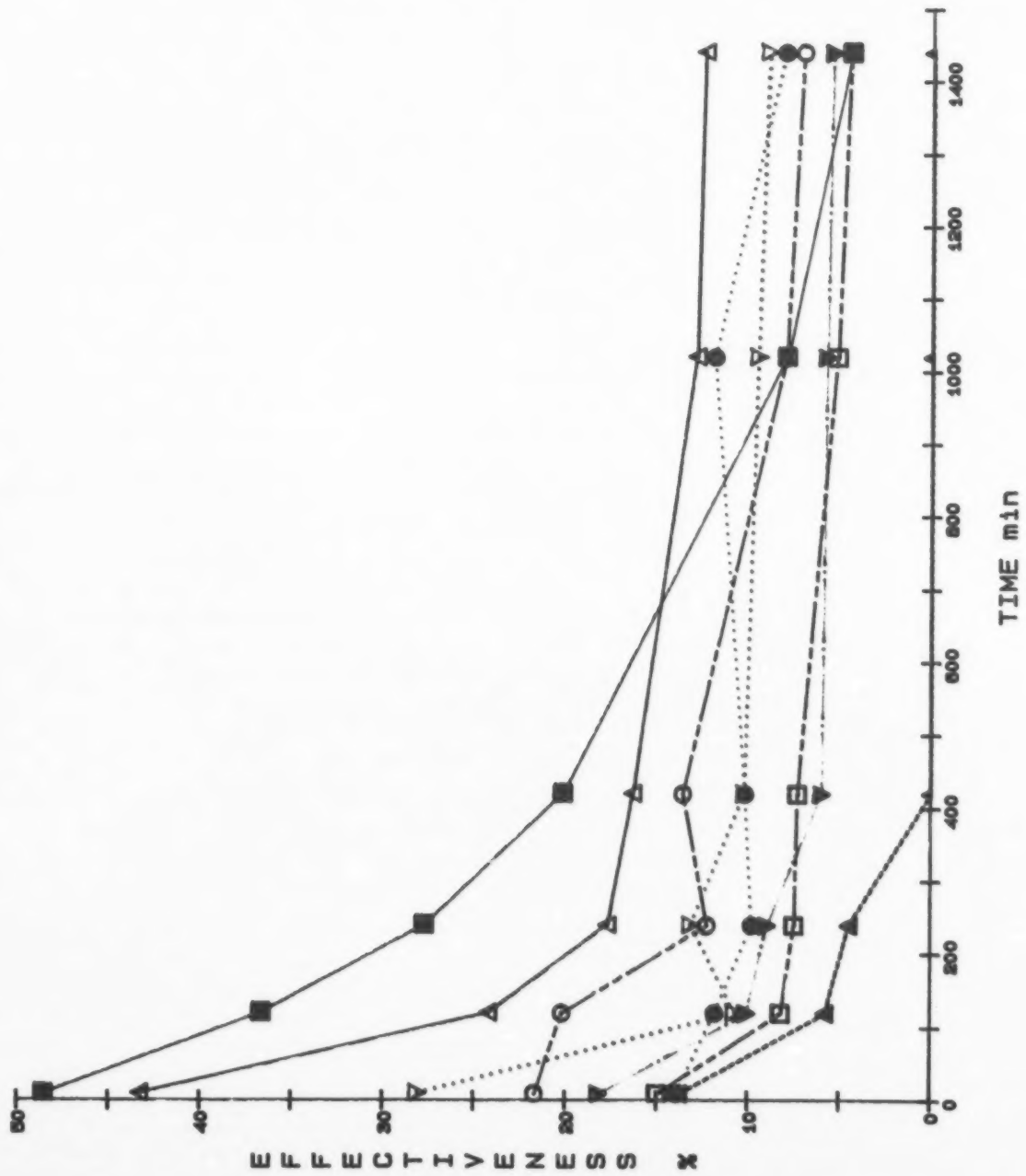
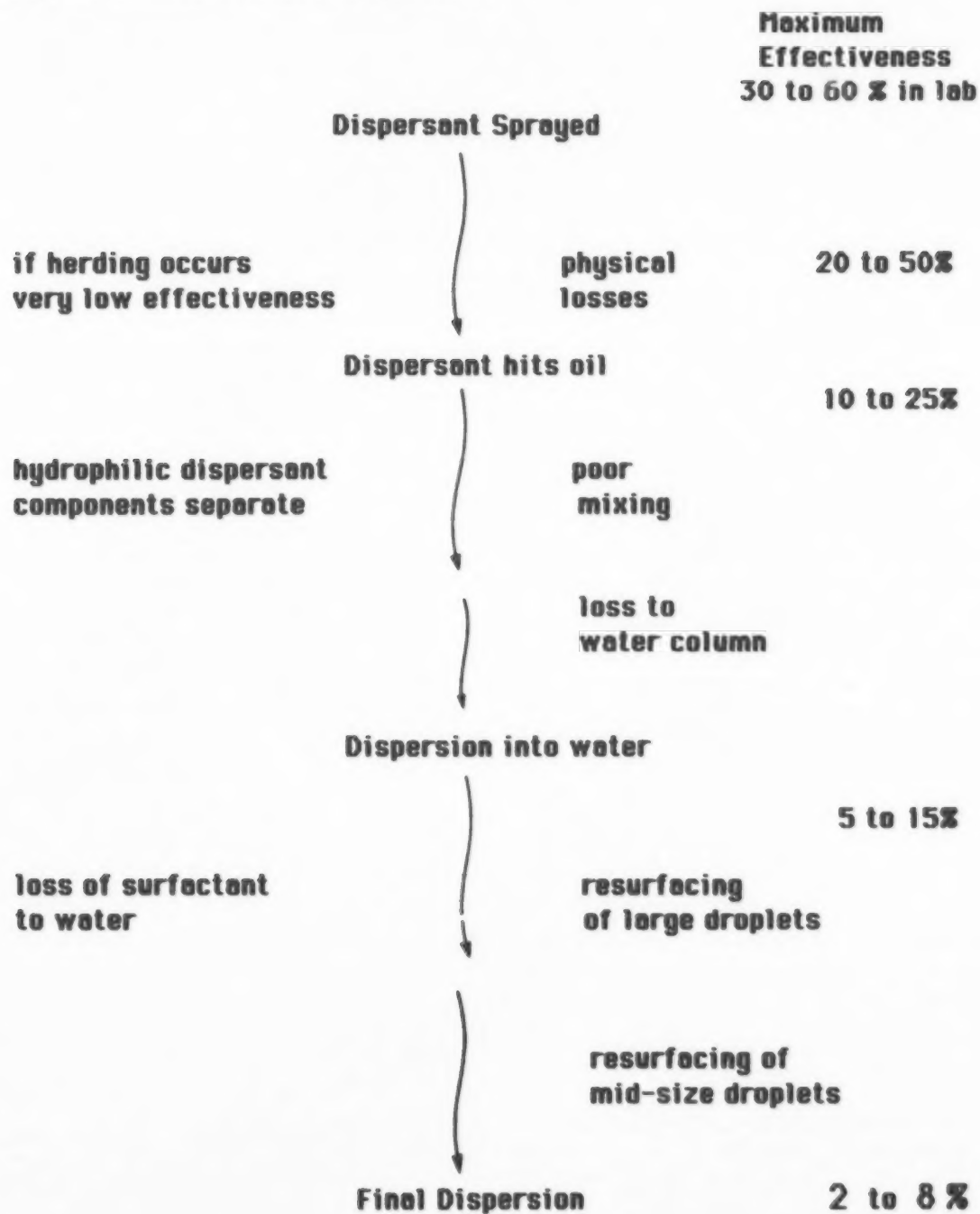
Figure 4
EFFECTIVENESS WITH TIME



Figure 5 Effectiveness in The Field



That being the case, dispersants which do not have the mixture of hydrophilic and hydrophobic dispersants may not cause herding and the accompanying loss of effectiveness;

2. sloughing-off loss - dispersants that contain the hydrophilic and lipophilic surfactant mixtures lose much of their effectiveness in the field by sloughing-off the hydrophilic components; and

3. less-leaching - present-day dispersants lose about half of their effectiveness by surfactant loss to the water, either before or after the dispersion process. This loss can be reduced by using more lipophilic surfactants, taking care not to promote the formation of water-in-oil emulsions.

To date, EETD has found a few compositions with improved characteristics. One of these yields a laboratory effectiveness of 100% and an estimated field effectiveness of 5 to 20%. This is about a 3-fold improvement over the best current commercial products. This development, although not a breakthrough, shows that some improvements can be made to existing dispersants.

Development on dispersants is difficult and laborious. First, analysis of surfactants either neat, in water or in oil, is difficult and actually impossible in some cases. Much work to date has involved direct effectiveness testing which is not precise and is very time-consuming. Secondly, both surfactants and oil are often complex mixtures and both can interact in unique ways. Testing is thus more difficult and less repeatable than one would normally expect. Thirdly, the HLB is not a good indicator of oil/water partitioning, leaving the choice of individual surfactant components rather arbitrary and experimental.

Conclusions

Current dispersants function poorly in field conditions. This lack of performance can be attributed to three processes which occur in field situations;

1. loss of surfactants at the water surface directly into the water column,

2. separation of mixtures containing surfactants of different HLB's and subsequent loss of the hydrophilic portions, and

3. loss of surfactant directly from dispersed oil droplets into the water column.

Limited research has shown that dispersants can be improved to raise their field effectiveness.

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A STUDY OF THE CHEMICAL DISPERSABILITY OF FRESH AND WEATHERED CRUDE OILS

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BACKGROUND

The study presented in this paper is a part of a three years research program called DIWO ("Application of Dispersants on Weathered Oils") presently running at IKU. The main objectives in this research program are:

- * to determine the "relative" dispersability of oils produced or transported in Norwegian coastal waters. Particular emphasis is placed on the role of oil weathering on dispersant effectiveness and to elucidate the "time window" for chemical treatment of different oils.
- * to study the formation and stability of w/o-emulsions as a function of oil type and degree of oil weathering.
- * to develop new dispersants with high performance on weathered oils.

This paper deals with the results of the chemical dispersability tests performed in the first part of the DIWO program. The preliminary results of the w/o-emulsion formation and stability study in the DIWO program are presented elsewhere in this volume (Daling and Brandvik, 1988).

INTRODUCTION

It is now widely accepted that chemical dispersants have a role in oil spill countermeasures, especially in near-shoreline situations where most of the damage will result from the presence of a surface slick which may foul birds and/or shorelines.

During the past 10 years, extensive studies have been carried out in order to assess the effectiveness of oil spill dispersants, both in the laboratory and in the field. Excellent literature reviews are available in e.g. Nichols and Parker (1985), Mackay et al. (1985) and Fingas (1987a and b). In many countries (e.g. Canada, France, Norway and the Netherlands) research programs have been carried out over a number of years.

Although much progress has been made, doubt still remains concerning the actual effectiveness of dispersants at sea under different conditions. One uncertain conclusion from these studies is that the dispersion process is very complex and poorly understood, and a basic appreciation of the dominant phenomena controlling dispersant effectiveness is still lacking.

Both the physical properties and chemical composition of an oil seem to have a pronounced effect on the effectiveness of a dispersant. However, so far, no simple chemical characterization of a crude oil is likely to be successful as a predictor of effectiveness (Mackay et al., 1985).

From an operational viewpoint it is essential to identify the types of crude oils which are dispersable or not by dispersants. Furthermore, it is still poorly understood how the changes in physico-chemical composition due to weathering of the oil at sea (e.g. evaporation, w/o-emulsion formation, photolysis) affect the performance of dispersants. The weathering issue has been largely ignored and it is appropriate to devote more attention to it in this paper.

During the past years, three laboratory dispersant effectiveness test methods have gained more general acceptance than others. Their basic principles and designs for e.g. producing mixing energy are very different. This means that they seem to simulate different "sea states" or conditions of use:

- * In the Labofina / Warren Spring Laboratory test (WSL-test, Martinelli, 1984) mixing energy is supplied by revolving flasks which gives a relatively high specific energy input. The mixing period is followed by a settling period of 1 minute before sampling (static sampling).
- * The IFP-test (Bocard and Castaing, 1987) is a low energy input test and is probably a more realistic approach because of the introduction of the dilution concept. The sampling is taken under dynamic conditions.
- * In the Mackay-Nadeau-Steelman test (MNS-test, Mackay and Szeto, 1980) energy is applied by blowing air across the oil/water surface, producing a circular wave motion. The energy input in this system corresponds more to a medium sea state condition. One sample of the oily water is taken under dynamic conditions and a second sample is taken after a settling period of 5 minutes (static conditions).

OBJECTIVES

The main objective of the study presented in this paper has been to define the overall chemical dispersability of three crudes (in both fresh and weathered conditions) produced or transported in Norwegian coastal waters. This has been obtained by:

- * evaluating and correlating the dispersant effectiveness results obtained in the three above mentioned laboratory test methods.
- * studying the relationship between the changes in dispersant effectiveness and the changes in the oils' physico-chemical properties due to different weathering processes (evaporation, photolysis and w/o-emulsification).

EXPERIMENTAL

The experimental procedures used are only briefly described below. A more detailed description of the procedures are given by Daling and Almås (1988).

Weathering procedures of oils

To isolate the effect of the different weathering processes (evapor-

ative loss, photolysis and w/o-emulsification), the weathering of fresh crudes was carried out using a systematic, step-wise procedure. Figure 1 shows a schematic diagram of the weathering procedure. The first step involved 3 different degrees of evaporative loss by a modified ASTM D86/82 distillation (Stiver and Mackay, 1984): The oil was topped at 150°C, 200°C and 250°C (vapour temperature) which roughly (depending on weather conditions) corresponds to 1 hour, 1 day and 1 week evaporative loss at sea respectively. Secondly, the fresh crudes were photolysed (artificial sunlight, cf. figure 2) for 1.5 and 20 hours. This caused an evaporative loss of the lightest components which was similar to the 200°C+ and 250°C+ topped fractions respectively.

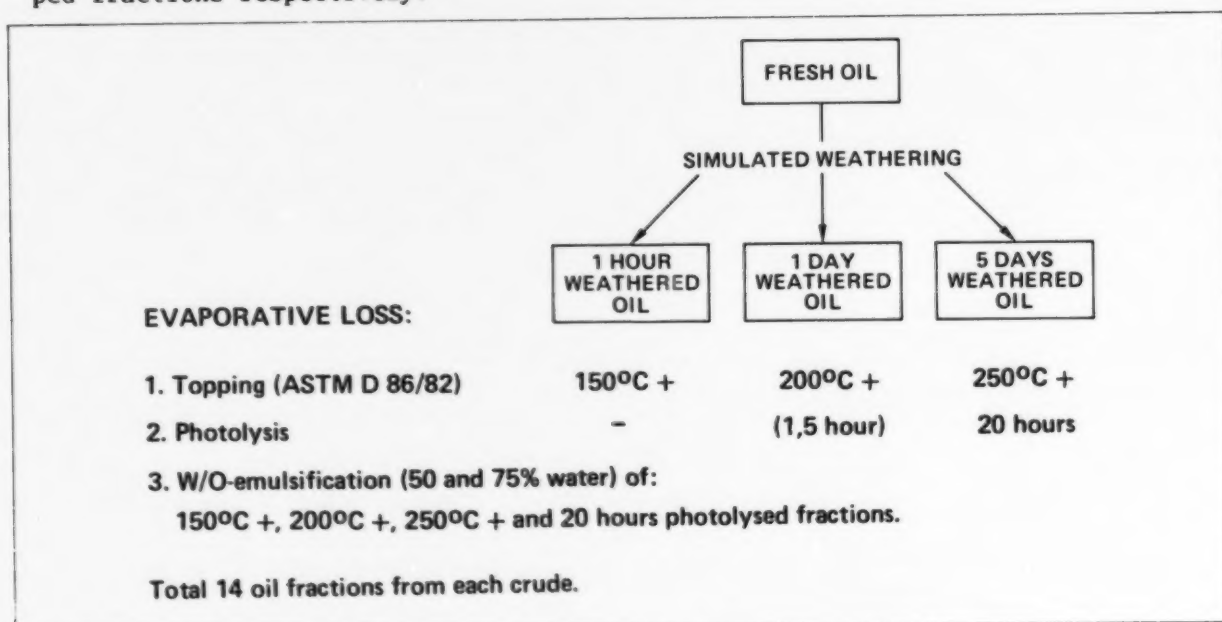


Figure 1. Schematic diagram of the oil weathering processes.

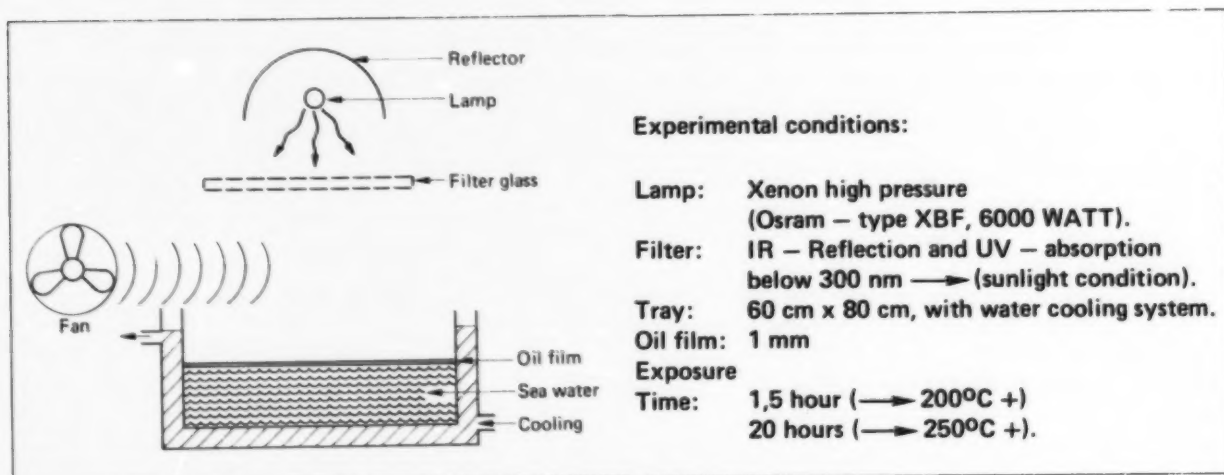


Figure 2. Schematic diagram of photolysis of the oil film.

Finally, the topped and the photolysed (20 hours) oil fractions were emulsified with 50% and 75% sea water (by mechanical stirring and dropwise addition of sea water to the oil, Daling and Almás, 1988).

Thus, 13 weathered fractions were prepared from each fresh crude which were all undergone physico-chemical analysis and chemical dispersability tests.

Physico-chemical analysis

The physico-chemical properties of the fresh, topped and photolysed oil fractions were characterised by the analytical methods listed below:

- Specific gravity: ASTM-method D4052-81
- Viscosity (dynamic): Haake Rotovisco RV3
- Pour point: ASTM-method D97-66 (IP-method 15/67)
- Flash point: ASTM-method D93-80 (IP-34/85)
- Interfacial tension: a) Pendant drop tensiometer
b) de Nouy ring method (ASTM-method 971-82)
- "Soft" asphaltene content: n-pentane insoluble (Daling and Almás, 1988)
- "Hard" asphaltene content: IP-method 143/84
- Wax content: Precipitation of deasphalted oil in
2-butanone/dichloromethane (1/1 vol) at
-10°C (Bridié et al., 1980)
- Sat., aro. and resin content: Iatroscan TLC/FID Chromatograph.

Dispersability testing

The dispersability of fresh and weathered oils was tested using the three laboratory test methods (WSL-, IFP- and MNS-tests). Additionally, a Malvern particle size analyzer (model 3600 Ec) was used to determine the size distribution of oil droplets present in the dispersions produced by the test methods.

The dispersability testing was carried out under the following conditions:

- Dispersants: Finasol OSR-5 (concentrate)
Finasol OSR-12 (conventional, HC based)
- Dispersant-to-oil ratio (DOR): 1/25 for OSR-5
1/2.5 for OSR-12

When testing the dispersability of w/o-emulsions, the dispersant-to-emulsion ratio (DER) was also 1/25 and 1/2.5 respectively.

- Temperatures (water and air): 6°C and 13°C (+/- 1°C)
(North Sea winter and summer conditions)

This paper deals mainly with the 13°C test results with Finasol OSR-5.

Types of crudes tested

The dispersant effectiveness tests were performed on fresh, topped, photolysed and w/o-emulsified oil fractions from the following three crude oils:

- Gullfaks crude: naphthenic, biodegraded North Sea Crude.
- Statfjord crude: paraffinic, wax-rich North Sea Crude.
- Arabian Heavy crude (Safaniya): viscous crude with a high content of heavy end components.

RESULTS AND DISCUSSION

Physico-chemical properties of oils and w/o emulsions

Crude oil is a complex mixture of hydrocarbons and non-hydrocarbons which commonly are classified into the following groups: saturates (e.g. alkanes and naphthenes), aromatics, resins (NSO-compounds) and asphaltenes (e.g. Mackay in 1987). Small differences in composition between different crudes can greatly affect the physical properties and hence the chemical dispersability of oil when spilled on water. Furthermore, the composition of the crudes is changed by weathering at sea.

The changes in chemical and physical properties with increased evaporative loss (topping), photolysis and w/o-emulsification are summarized in tables 1 and 2.

Gullfaks crude is a naphthenic North Sea crude. The high degree of biodegradation has resulted in a low content of n-alkanes and a low wax content which gives very low pour points (see tables 1 and 2). The low paraffin content may also explain the relatively high density of Gullfaks crude compared to more common paraffinic North sea crudes. The resin and asphaltene content of the Gullfaks crude is at the same low level as in most of the North Sea crudes.

Statfjord crude is a typical paraffinic North Sea crude with low density, low resin and low asphaltene content. Statfjord crude has a relatively high wax content which may explain the high pour point values (table 2).

Arabian Heavy (Safaniya) crude is imported to Norwegian refineries and is characterized by high density, high viscosity and high content of heavy end components (e.g. resins and asphaltenes). This crude is completely different from the crudes produced from the North Sea.

Photolysis. Photolysis has a significant effect on some of the physico-chemical parameters of the oils: The photolysed (20 hours) fractions have significantly higher resin and asphaltene contents compared to the corresponding 250°C+ topped fractions (see table 1 and figure 3a). Figure 3a shows that aromatics (but probably also naphthenes in the Gullfaks crude) have been photo-oxidized to more polar components (resins). The photolysis may also lead to photo-polymerization (Daling, 1984), which may explain the observed increase in asphaltene content (table 1).

Among the physical parameters, interfacial tension is particularly affected by photolysis. There is a drastic reduction in the interfacial tension for both the 1.5 and 20 hours photolysed fractions (see figure 3b), which clearly demonstrates the formation of surface-active components by photolysis.

The photolysed (20 hours) fractions show a slightly higher viscosity compared to the corresponding 250°C+ topped fractions (particularly the Arabian Heavy, table 2). One reason for this may be photo-polymerization

Table 1:
Chemical properties of fresh and weathered crude oils used in the experiments.

Oil type	Saturates ¹⁾ (wt.%)	Aromatics ¹⁾ (wt.%)	Resins ¹⁾ (wt.%)	Asphaltenes (wt.%) ²⁾		Waxes ³⁾ (wt.%)
				"hard"	"soft"	
GULLFAKS:						
Fresh	-	-	-	0.02	0.49	1.60
150°C+	-	-	-	0.02	0.52	1.72
200°C+	-	-	-	0.03	0.58	1.90
250°C+	52.1	40.0	6.8	0.03	0.65	2.14
20. h. ph.ox (250°C+)	45.3	37.8	15.3	0.24	1.11	-
STATFJORD:						
Fresh	-	-	-	0.01	0.39	4.14
150°C	-	-	-	0.01	0.47	4.78
200°C+	-	-	-	0.02	0.54	5.77
250°C+	56.2	34.8	7.8	0.02	0.63	6.68
20. h. ph.ox (250°C+)	59.5	25.6	13.7	0.29	1.14	-
ARABIAN HEAVY:						
Fresh	-	-	-	4.33	7.38	4.62
150°C+	-	-	-	4.89	8.34	5.22
200°C+	-	-	-	5.31	9.05	5.67
250°C+	23.2	49.0	18.4	5.80	9.89	6.19
20. h. ph.ox (250°C+)	23.6	41.4	23.6	7.21	10.42	-

¹⁾ Quantification by Iatroscan TLC/FID

²⁾ Asphaltene content is calculated from data of the 250°C+ fraction, "hard" asphaltenes: IP-143 method, "soft" asphaltenes: n-pentan insoluble.

³⁾ Wax content is calculated from data of the malthe fraction of 250°C+ (after the "hard" asphaltene separation)

Table 2:
Physical properties of fresh and weathered crude oils used in the experiments

Oil type	Evapor. loss (Vol.%)	Spec.grav. (g/ml) (15.5°C)	Pour point (°C)	Interf. tension (mN/m)	Viscosity of oil and w/o-emulsions ¹⁾ (cP at 13°C)		
					0% Water	50% Water	75% Water
GULLFAKS:							
Fresh	-	0.882	<-34	13	20	-	-
150°C+	8	0.893	-26	13	33	440	1780
200°C+	18	0.905	-15	15	72	800	4980
250°C+	28	0.914	-9	17	241	1780	6760
1.5 h. ph.ox (200°C+)	18	0.906	-	2.7	87	-	-
20. h. ph.ox (250°C+)	28	0.916	-	1.1	282	2300	92700
STATFJORD:							
Fresh	-	0.834	-15	23	7	-	-
150°C+	20	0.867	7	16	20	160	1200
200°C+	32	0.882	11	15	57	490	3560
250°C+	42	0.895	16	16	221	1800	4600
1.5 h. ph.ox (200°C+)	32	0.883	-	5.4	77	-	-
20. h. ph.ox (250°C+)	42	0.896	17	1.0	314	16870	43600
ARABIAN HEAVY:							
Fresh	-	0.887	-28	20	41	-	-
150°C+	15	0.920	-23	14	241	4800	93000
200°C+	23	0.935	-18	18	700	16870	- ²⁾
250°C+	30	0.951	-5	17	2344	43600	- ²⁾
1.5 h. ph.ox (200°C+)	23	0.935	-	4.9	725	-	-
20. h. ph.ox (250°C+)	30	0.954	-	1.1	4350	4350	120000

¹⁾ Measured at a shear rate = $10s^{-1}$ for viscosities below 10000cP and $1s^{-1}$ for viscosities above 10000 cP.

²⁾ Emulsion not possible to prepare.

which may take place. Other physical properties like the pour point and density do not seem to be significantly influenced by photolysis.

W/O-emulsions. All the topped and the photolysed (20 hours) fractions of the three crudes were emulsified (with 50% and 75% sea water) for dispersability testing and viscosity measurements (table 2). An example of a plot

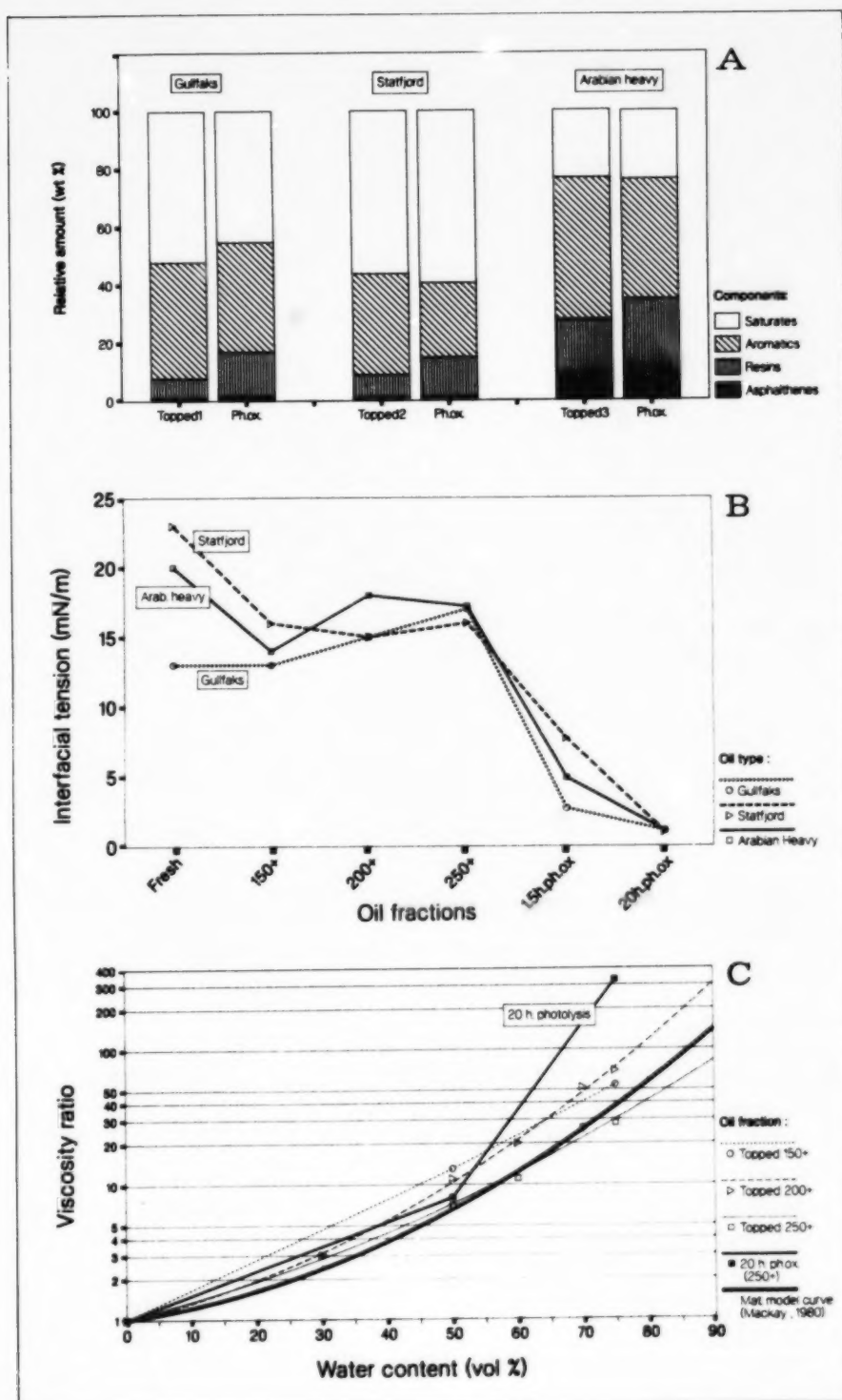


Figure 3. Physico-chemical changes due to weathering.
 a) The effect of photolysis on chemical composition (quantified by Iatroscan TLC/FID).
 b) Interfacial tension.
 c) Viscosity ratio between w/o-emulsion and parent oil versus water content.

of the viscosity ratio between the w/o-emulsion and parent oil (μ / μ_o) versus water content is given for the different fractions of Gullfaks crude in figure 3c. The figure clearly illustrates the increase in viscosity ratio, which is especially marked when the water content exceeds 50%. Figure 3c also includes the existing mathematical model equation of the viscosity ratio developed by Mackay et al. (1980). There is a fairly good correlation between the model equation of Mackay et al. and experimental values, although the experimental data obtained at IKU tend to be slightly higher. One reason for this may be that the empirical model of Mackay et al. is based on viscosity measurements of w/o-emulsions applied at much higher shear rates (1180 s^{-1}) than the IKU results (1 and 10 s^{-1}).

An interesting observation from figure 3c is that the photolysis seems to have a significant influence on the viscosity of the w/o-emulsions. This applies especially to the w/o-emulsions with water contents of greater than 50%, where the viscosity ratios of the photolysed (20 hours) fractions increase much more rapidly (up to 10 times higher viscosity ratio) than the corresponding $250^\circ\text{C}+$ topped fractions. It is believed that the low interfacial tension in the photolysed oils results in w/o-emulsions with smaller water droplets which leads to a higher viscosity of the w/o-emulsion. This agrees with the results obtained from the w/o-emulsion formation and stability study using the rotating flask method (Daling and Brandvik, 1988, this volume) where the w/o-emulsions of the photolysed oils showed a much higher stability and slightly smaller water droplets than the corresponding non-photolysed w/o-emulsions.

Chemical dispersability of fresh and weathered (water free) oils

Droplet size distribution in the test methods. The Malvern particle size analyzer was used to characterize the oil droplet size distribution in all the dispersions produced in the test methods. Figure 4 shows that both the median droplet size ($D_{50\%}$, defined as the droplet diameter at which 50 vol% of the oil consists of droplets less than $D_{50\%}$) and the droplet size distribution (expressed by the Span = $(D_{90\%} - D_{10\%}) / D_{50\%}$) are significantly different in the 3 tests. This reflects the different design (particularly the energy input and the sampling procedure) of the methods. In the systems with static sampling (WSL and 2nd MNS), the settling time (of 1 and 5 min. for the two methods respectively) allows the largest oil droplets above the critical diameter for resurfacing to float out of the sample zone in accordance with Stokes law. This results in smaller values for both the $D_{50\%}$ and the Span.

How reliable is the WSL-test? The WSL-specification (Morris and Martinelli, 1983) of the Labofina (inverting flask) method has been adapted by several governments for dispersant approval test purposes. The WSL-test is simple and rapid and shows good reproducibility. The unnaturally high regime of energy input during mixing in the WSL-test has, however, often been criticized (eg. Gillot et al, 1987, Lewis et al., 1985). Furthermore, due to the settling period of 1 minute before sampling, the WSL-test is very sensitive to the resurfacing velocity of oil droplets, and thus tends to give good performance for dense oils (Mackay et al., 1985). This was also observed from our effectiveness results for the water-free oil fractions. The results suggest a relatively high dispersability for the Arabian Heavy oil fractions, while the light crudes (e.g. Statfjord fractions) gave low effectiveness values (below 20%, figure 5a). As discussed by e.g. Martinelli and Lynch (1980), this increase in effectiveness with increased topping

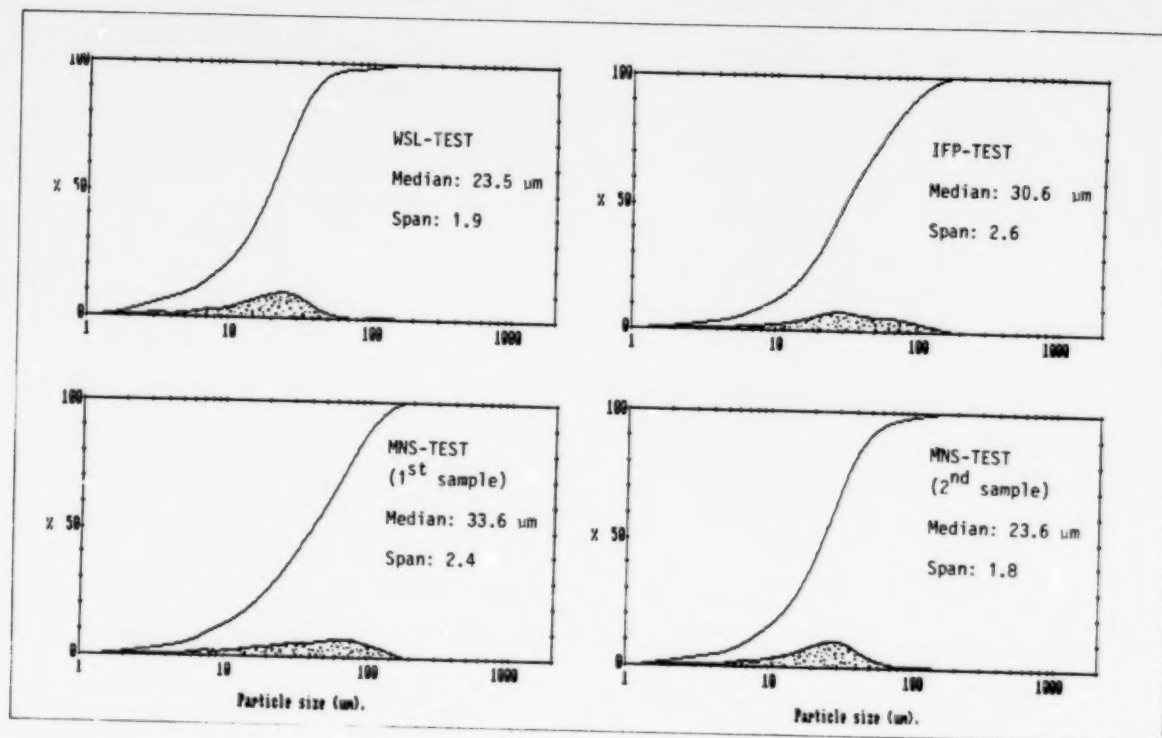


Figure 4. Example of the median droplet size (μm) and droplet size distribution (span) in the different test methods (Gullfaks 150°C+, treated with Finasol OSR-5 at 13°C).

(figure 5a) can also be explained by the increase in density of the oil.

The close correlation between an oil's density and dispersability in the WSL-test is shown in figure 5b (fresh and topped oil fractions, at 13°C).

Another effect which has hitherto been largely ignored, and which may explain the low performance for many crudes, in spite of the large mixing energy used in the WSL-test, is the high relative volume of oil (5 ml oil to 250 ml sea water = 2 vol%) compared with other laboratory test methods. This effect has only been briefly discussed by Mackay and Chau (1987) and Lewis et al. (1985). Figure 5c shows how the effectiveness depend on amount of oil used in the system (the dispersant-to-oil ratio has been kept constant, DOR = 1:25, premixed). The reduction in effectiveness which arises when the oil concentration in the water column reaches around 0.1-0.5% (= 0.2-1 ml oil in the system), is probably due to droplet interaction (coalescence) which seems to increase strongly. The drop in effectiveness with increased amount of oil is naturally more drastic for the relatively light Gullfaks and Statfjord crudes compared with the denser Arabian Heavy crude (figure 5c).

These limited number of tests indicate therefore that the standard amount (5 ml) of oil used in the WSL-test is far too high (relative to the volume of sea water) and this leads to low and unreliable effectiveness results.

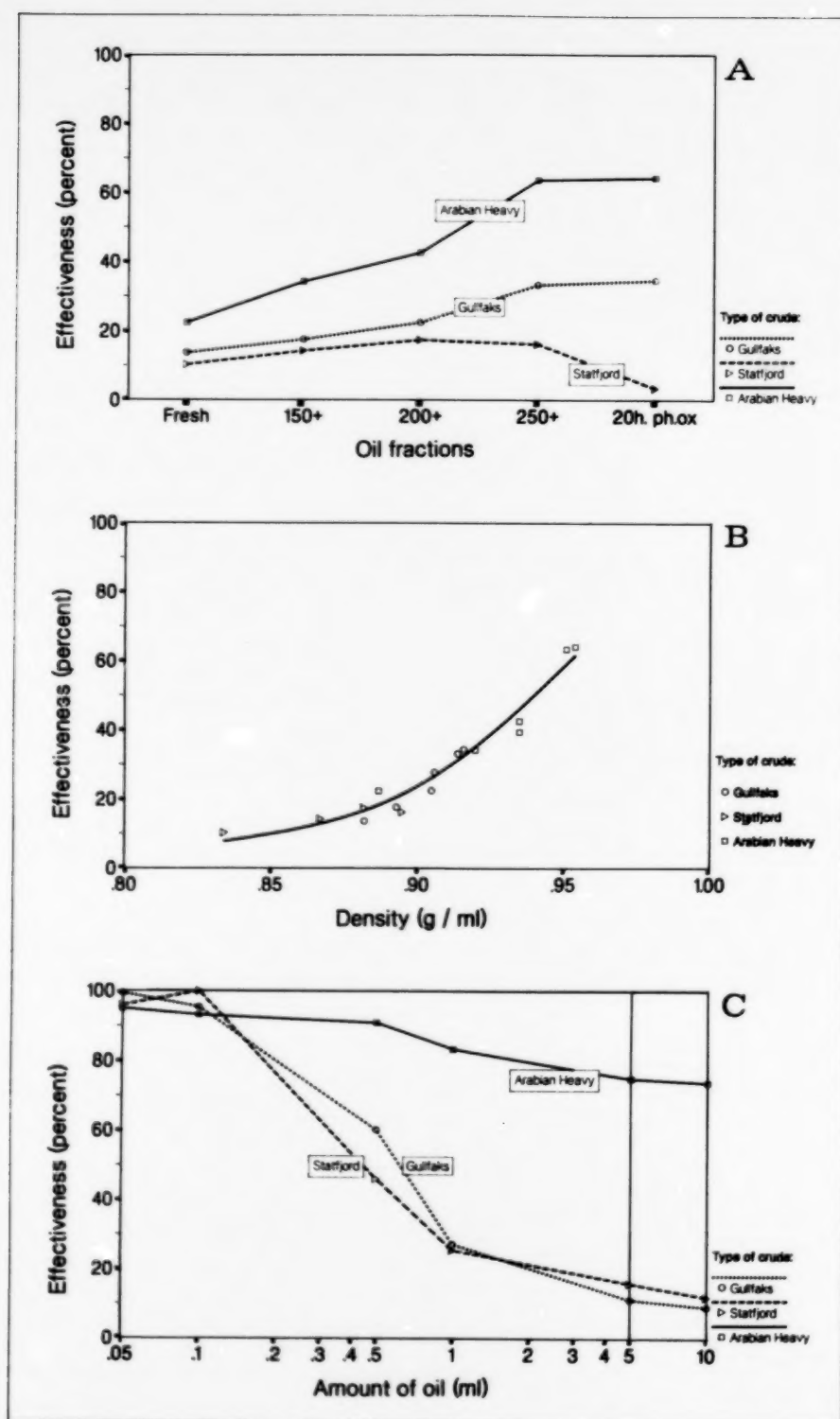


Figure 5. Effectiveness results in the WSL-test (Finasol OSR-5 at 13°C):
 A) Fresh and weathered oil fractions of Gullfaks, Statfjord and Arabian Heavy crudes (standard WSL-test procedure).
 B) The dependence of oil density (fresh and topped fractions).
 C) The dependence of amount of oil used in the WSL-rotating flasks (Gullfaks, Statfjord and Arabian Heavy 150°C+ fractions, dispersant premixed DOR = 1:25).

The IFP- and MNS-test results. Figures 6a and b show dispersant effectiveness on the fresh and weathered oils at 13°C. In the IFP and the 1st sampling of MNS-tests there is no typical increase in effectiveness with increased weathering (topping) within the same oil type. This indicates that these two methods, where the samples are taken under dynamic conditions, do not seem to be so sensitive to oil density, but that other parameters (oil type, weathering, temperature etc) may have a greater influence on dispersant performance. Figures 6a and b show that IFP- and the MNS-tests (dynamic sampling) give similar results. The MNS-test, however, indicates relatively higher effectiveness on viscous oils (Arabian heavy) and for oils close to their pour point (topped Statfjord oils). This may be explained by a higher surface turbulence in the MNS-test compared to the IFP-tests. The 2nd MNS sampling results (not presented here) show low effectiveness values (15-30%) and relatively low selectivity between the oils (similar results as in the WSL-test).

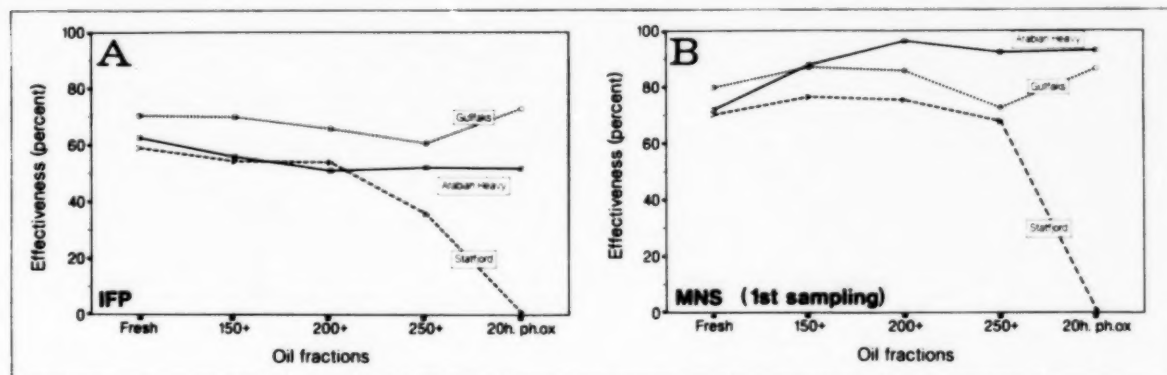


Figure 6. Chemical dispersability of fresh and weathered (water-free) oils (by Finasol OSR-5 at 13°C)
a) IFP-test,
b) MNS-test (1st sampling results).

The influence of photolysis. The effects of photolysis were similar as measured by all the three test methods, but most were apparent in the IFP and MNS-tests (figures 6a and b).

Photolysis affects the dispersability of the three crudes in very different ways:

Gullfaks: Slight increase in effectiveness after photolysis.

Statfjord: Drastic reduction in effectiveness after photolysis.

Arabian heavy: No significant influence.

The contrary effect of photolysis on the dispersability of the different crudes has to be connected to the different chemical composition of the crudes. The increase in effectiveness for the photolysed Gullfaks crude may be explained by the formation of surface-active compounds by photolysis which appear to act as dispersants (lowering the interfacial tension from

15 to 1 mN/m, figure 3b).

For the paraffinic and wax-rich Statfjord crude, however, there is a drastic reduction in dispersability when the oil is photolysed. One explanation for this contrary effect compared to the Gullfaks crude, may be that the surface-active photolysed products in the Statfjord oil facilitate wax accumulation at the o/w-interface which "block" access of dispersant surfactants to the interface. This is in accordance with the earlier hypothesis postulated by Mackay and Chau (1987).

For the Arabian heavy, the amount of photolysed components produced is probably so low relative to the natural film-forming components (resins and asphaltenes, see table 1), that no significant effect of photolysis is observed (e.g. figures 6a and b).

The effect of pour point. The pour point of an oil is defined as the temperature below which the oil will not flow (measured under standardized and static conditions in the laboratory) due to crystallization of waxes. It has often been considered that, if the ambient sea temperature is below the pour point of the oil, then the oil is no longer chemically dispersable. Wax crystals appear to reduce the ability of the dispersant to access and mix into the oil (Mackay et al., 1985).

It is, however, important to notice that the turbulent condition at the sea surface may retard agglomeration of the waxes crystal.

We have observed in our study that the drop in dispersant effectiveness which may arise, when approaching the pour point (e.g. for the topped fractions of Statfjord crude) is different in the different test methods. This difference seems to reflect the relative turbulence of the water surface in the tests: WSL > MNS > IFP (Lewis et al., 1985, Gillot et al., 1987). The relatively high surface turbulence in the WSL-test is therefore probably the reason why that method is not particularly sensitive to the pour point of the oil (oils are dispersable to typically 10°C below pour point).

The IFP-test appears, however, to be very sensitive to the pour point of the oils, which is probably due to the relatively low surface turbulence in this test. This means that oils with high pour points (e.g. the Statfjord fractions) will solidify more easily on the water surface in the IFP-test compared to the WSL-test. The MNS-test has a somewhat more turbulent surface during the mixing process than the IFP (but not as turbulent as the WSL-test), permitting dispersion of oils about 5°C below their pour point.

The effect of temperature. The results presented in this paper are all performed at 13°C (North Sea summer conditions). A similar study performed at 6°C (North Sea winter conditions) has shown only a slight reduction in dispersant effectiveness (typically 0-20% lower effectiveness values).

This is in accordance with Mackay et al. (1985), who typically found a halving of effectiveness, or a doubling of the dispersant dosage was required to achieve a defined performance over the temperature range 25°C to 0°C. As concluded earlier by Mackay et al. (1985), the dispersion is likely to require more dispersant under cold conditions, but this extra amount is unlikely to be large except when the oils are unusually viscous or close to their pour point.

In our test the WSL-test proved to be least temperature-dependent, and the IFP-test was most temperature-sensitive.

Dispersability of w/o-emulsions

The figures 7a-c summarize all the effectiveness results (with Finasol OSR-5 at 13°C) on the water-free fractions and 50% and 75% w/o-emulsions of the three crudes, all plotted as a function of the oil or w/o-emulsion viscosity.

The upper limit for dispersability according to the viscosity of the w/o-emulsion seems to be very specific for each type of crude:

Gullfaks: A drastic drop in dispersability for w/o-emulsions around 6000-8000 cP (at 10 s^{-1}) in all three test methods.

Statfjord: For this "pour point problem" oil, the upper limit for dispersability depends on test method used:

WSL: drop in dispersability around 2000-3000 cP.

IFP: drop in dispersability around 300-500 cP.

MNS: drop in dispersability around 1500 cP.

(all measured at 10 s^{-1}).

Arabian heavy (only 50% w/o-emulsions):

Slight drop in dispersability above 20000 cP, however, in the WSL and MNS, w/o-emulsions over 40000 cP (at 1 s^{-1}) are still dispersable.

All three test methods agree fairly well (except for Statfjord) in defining this upper limit of dispersability according to the viscosity of each crude. In spite of fairly good agreement between the tests, it was possible to detect some systematic difference which seems to reflect the relative energy input in each test method: The drop in dispersability of the w/o-emulsions with increased viscosity appears earlier in the IFP-test, while in the WSL-test the drop appears at a slightly higher viscosity. This difference was most apparent with the Statfjord w/o-emulsions due to their pour points (discussed earlier).

The results obtained above indicate therefore that it is not possible to use e.g. 2000 (or 5000) cP as a general rule for the upper limit of dispersability according to the viscosity of w/o-emulsions. Therefore, it seems that the viscosity is not the only parameter which controls the dispersability of viscous w/o-emulsions.

One important factor is probably the ability of the dispersant to break the w/o-emulsion (e.g. Ross, 1986, Daling and Brandvik, 1988). An interesting observation can be made from figure 8, where the dispersant effectiveness of the 50% w/o-emulsions of Gullfaks crude show very similar dispersability to the parent (water free) oils. Furthermore, the droplet size of the dispersions made from the parent oils and from the w/o-emulsions are also similar (30-60 μm , figure 8b). This means that there is no space for water droplets (typically 10-50 μm) in the dispersed oil particles.

It is therefore believed that the mechanisms for chemical dispersion of w/o-emulsions pass through the following two steps:

- Step 1:** The dispersant breaks the w/o-emulsions into oil and free water.
- Step 2:** The water-free oil is dispersed as small oil droplets into the water column.

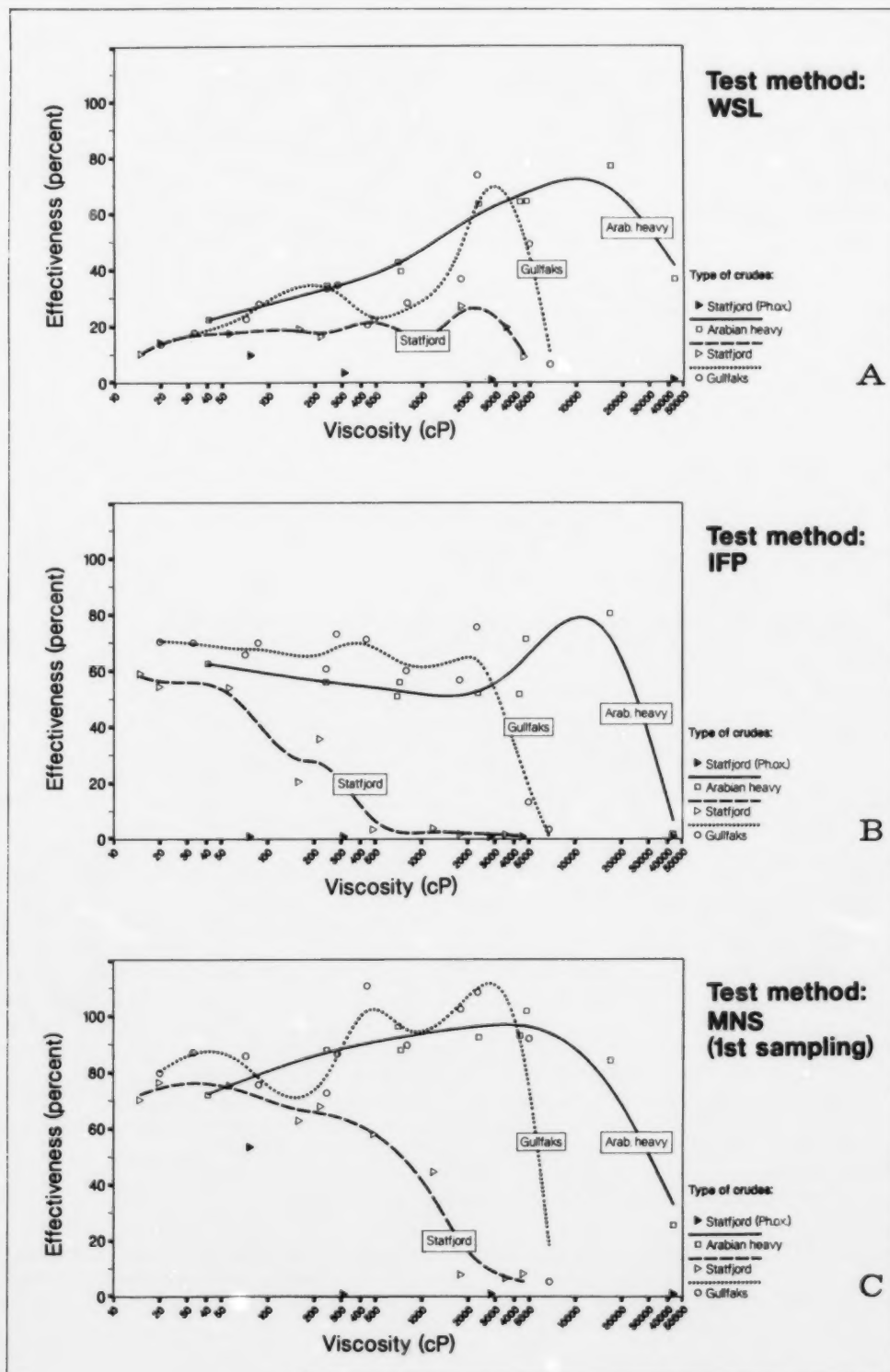


Figure 7. Dispersability of crude oils and their 50% and 75% v/o-emulsions versus viscosity of the oils and v/o-emulsions (measured at shear rates 1 or 10 s^{-1}).

Step 1 is probably the limiting factor, as the dispersant has to access and mix into the viscous w/o-emulsions. Once the w/o-emulsion has been broken, the viscosity of the water free oil becomes several times lower than the w/o-emulsion (figure 3c). The water-free oils are therefore usually easily dispersed into the water column if sufficient amount of dispersant is still present in the oil.

The very similar dispersability results between parent oils and 50% w/o-emulsions (figure 8a) indicate that, for a w/o-emulsion containing 50% sea water, typically half of the dispersant is consumed in breaking the w/o-emulsion (and then probably lost to the water-column), while the remaining amount of dispersant in the oil is used to disperse the water-free oil into the water.

The low dispersability results of the 75% w/o-emulsions (figure 8a) indicates that the dispersant is not able to break w/o-emulsions with viscosities above 6000-8000 cP containing 75% water. On the other hand, the dispersant is able to break and disperse w/o-emulsions of Arabian Heavy with viscosities of 40000-50000 cP (shear rate $=1s^{-1}$, figure 7). These w/o-emulsions contained, however, only 50% water.

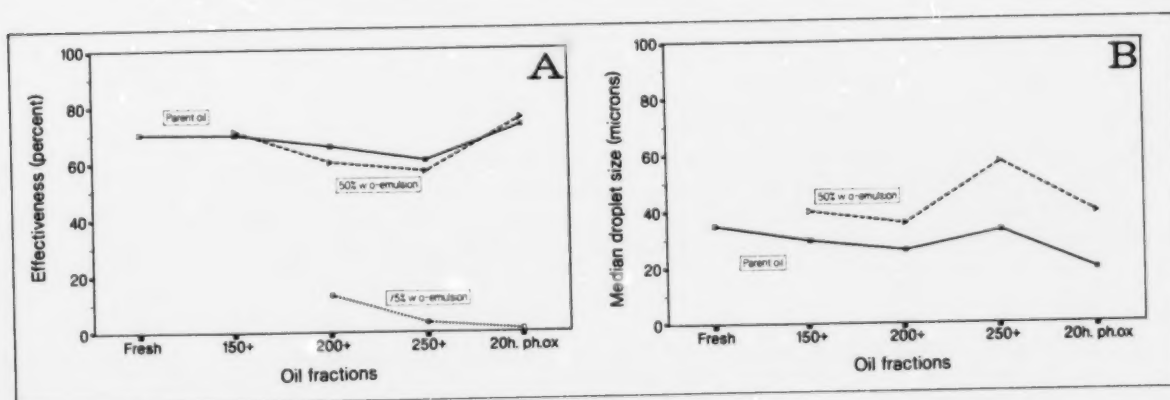


Figure 8. Dispersability test results from the IFP-test of parent oil and w/o-emulsions of Gullfaks crude treated with Pinacol OSR-5 at 13°C.

a) Dispersant effectiveness, b) Median droplet size.

SUMMARY AND CONCLUSIONS

An extensive laboratory study has been carried out to establish the dispersability of different crudes. Particular emphasis has been placed on revealing the role of different types of weathering on the dispersant effectiveness in the different laboratory test methods:

- * The results obtained clearly demonstrate that the three test methods are measuring different phenomena, which may reflect their completely different designs:

WSL-test:

This method is very sensitive to resurfacing velocity of oil droplets and thus tends to give high performances for dense oils. For light crudes, the method gives low effectiveness values. One important parameter here is probably the high relative volume of oil in the system where interaction and coalescence of oil droplets leads to low and unreliable results. Furthermore, high surface turbulence during the mixing permits dispersion of oils at temperatures up to 10°C below their pour point temperatures.

IFP-test:

This method appears to be the most selective and most sensitive of the three laboratory methods according to e.g. type of dispersant, oil qualities and weathering effects. Due to the low energy and turbulence on the surface, the method is especially sensitive to oils that are unusually viscous or close to their pour points.

MNS-test:

The first sampling (dynamic) of MNS showed effectiveness results according to oil type and weathering effects which are quite similar to the IFP results. Second sampling (static) results were close to the WSL results. The energy input in the MNS-tests seems to lie somewhere between the two other laboratory methods.

- * In spite of great variations in the effectiveness results between the different test methods used, they agree fairly well in ranking the dispersability of the different crudes. The droplet size measurements gave valuable information about dispersability, in addition to effectiveness values.
- * Photolysis had a tremendous effect on oil properties:
 - significant increase in resin and asphaltene content
 - drastic reduction in interfacial tension
 - formed w/o-emulsions with 3 - 10 times higher viscosity compared to corresponding non-photolysed oils.
- * Photolysis affected the chemical dispersability of the oils in very different ways:
 - Naphthenic crudes (e.g. Gullfaks) were enhanced by photolysis
 - Waxy crudes (e.g. Statfjord) lost their dispersability drastically after photolysis (photolysed components seem to facilitate accumulation of waxes at the w/o interface, which "block" the access of dispersants).
- * The dispersability of an oil is only slightly influenced by temperature (typically 0 - 20% reduction in effectiveness between 13 and 6°C), unless the oils are unusually viscous or are close to their pour points.
- * The limitation in dispersability of w/o-emulsions with increased visco-

sity of the w/o-emulsion is somewhat different for the three test methods, and seems to reflect the specific energy input of the methods (the viscosity limit for the WSL-test is slightly higher than e.g. for the IFP-test).

- * The viscosity limit for the dispersability of w/o-emulsions seems to be very specific for the different crudes. This means that it does not seem possible at present to give a general rule concerning the upper viscosity limit for dispersability of w/o-emulsions. A dispersant's ability to break the w/o-emulsion before the oil is dispersed into the water column seems to be the limiting factor.

RECOMMENDATIONS

This study clearly demonstrates that the type of crude, and especially the weathering properties of the crudes, is essential in determining the performance of dispersant at sea. From an operational point of view, it is very important to perform, in the near future, a series of dispersability tests on a number of oils in a similar way to this study. This kind of information will afford valuable data input to the improvement of existing models for estimating the weathering of oils at sea and especially to elucidate the "time window" for chemical dispersion of specific crudes under different weather conditions. At that stage, the use of dispersants will move to a much more advanced state of predictability and reliability.

ACKNOWLEDGEMENTS

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DISPERSANT TESTS IN A WAVE BASIN**-FOUR YEARS OF EXPERIENCE-**

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INTRODUCTION

Wave basin tests of dispersants, using a variety of oils, have been carried out over a four year period by Esso Resources. The tests were initiated when it became clear that the effectiveness of dispersants, as measured in common laboratory tests, did not appear to reliably predict the dispersion of oil in field trials (Nichols and Parker (1985), Fingas (1985)). The laboratory tests used to characterize dispersant chemicals have themselves been carefully studied in recent years and the physical processes involved in each are now better understood (Lewis et al (1985)). In essence, however, no laboratory test effectively reproduces all of the complex physical processes occurring during dispersion at sea. In a large wave basin, on the other hand, it was felt that the processes of dispersion would be essentially the same as those on any large body of water.

A variety of measurement techniques have been used during these wave basin tests to study the physical processes of dispersion and to determine the effectiveness of the dispersant. More than 40 oil spills with a volume of 75 litres each have been made. These spills have involved four different oils at various stages of weathering, four dispersants, salt water temperatures ranging from -2°C to 8°C, several wave energies, and three different dispersant application techniques. This paper will describe the development of the measurement strategies and some of the results of these studies.

EXPERIMENTAL DESIGN

The wave basin at Esso's laboratory in Calgary has been described in detail elsewhere (Brown et al (1985)). It is essentially a large outdoor concrete pool with wave making and refrigeration facilities.

Over the course of four years of tests, a number of different experimental procedures have been followed with a variety of measurements employed. Typically, oil has been spilled into a floating circular boom, sprayed in some manner with a dispersant, and then subjected to wave action over a period of hours. During this time, the oil slick has been sampled, overhead photographs and videos of the slick have been taken, and oil in the water column has been monitored. These measurements have been directed at answering two important questions:

What is the effectiveness of a particular dispersant on an oil in cold saline water such as the Beaufort Sea?

What are the processes which appear to make dispersants behave differently in laboratory tests and in ocean spills?

The experimental procedures used to obtain as much information as possible on each aspect of the dispersion process are described in the following sections.

Dispersant Application

In an ocean spill, the dispersant would likely be applied as a spray from the air. In the wave basin this process should be simulated as closely as possible. Some mechanism of controlling the dispersant drop size distribution is also desirable so that drops are large enough to prevent drifting but not so large as to break through the oil layer. The dispersant must be applied at a uniform rate even though the oil slick may vary in thickness and may not completely cover the sprayed area. Some method is needed of determining the application rate and the amount that has either penetrated the oil layer or missed it completely. Surfactants which enter the water may cause oil herding.

The apparatus shown in Figure 1 was built to spray dispersant uniformly onto the oil spilled within a circular containment boom. It consists of a tower attached to the basin floor with a 5m long rotating arm at its top. The height of the arm above the tower base can be adjusted and is usually set to be 1m above the water level. Spray nozzles are mounted along the bottom of the arm at a spacing which will give uniform coverage as the arm rotates. Each of the nozzles can be turned on or off independently from a remote control panel. Dispersant is piped from a reservoir to each nozzle through identical lengths of tubing. Spraying rate and drop size distribution are controlled by varying the air pressure in the dispersant reservoir with a compressor.

A 17m high scaffolding tower was constructed at one edge of the oil containment boom to serve as an observation post (Figure 2). The spraying apparatus was controlled by a technician on the tower from a position where he had an unobstructed view of the oil slick surface. A rail was extended from the top of the tower to the centre of the spill area. Remotely controlled cameras were mounted on a trolley which could be pulled along the rail to a position directly over the spilled oil. Thirty-five millimetre photographs and videos taken from this position were used to determine the dispersant dosage rate and to observe any oil herding. Thick oil areas in photographs taken during the spraying operation were measured with an image processing system.

To check the efficiency of the rotating arm sprayer, the dispersant was applied with a small hand-held sprayer from a boat in a few tests. This insured that all of the chemical was applied only to thick oil and that the spray was fine enough that no drops broke through the oil layer.

Dispersant/Oil Interaction

The type of oil, the degree of oil weathering, the oil thickness, the water salinity, the dispersant hydrophilic-lipophilic balance, and other factors will determine the amount by which the dispersant will lower the oil/water interfacial tension. Many of these factors are best studied in a laboratory. However, the weathering of an oil in situ before the dispersant is applied must be determined in order to compare one test to another. A technique using simulated distillation gas chromatography has been used to determine the extent of oil weathering from a small sample of oil. Dispersant effectiveness as a function of weathering (or of viscosity if a relationship is known) can then be measured.

Key to Photographs on Following Page

Figure 2

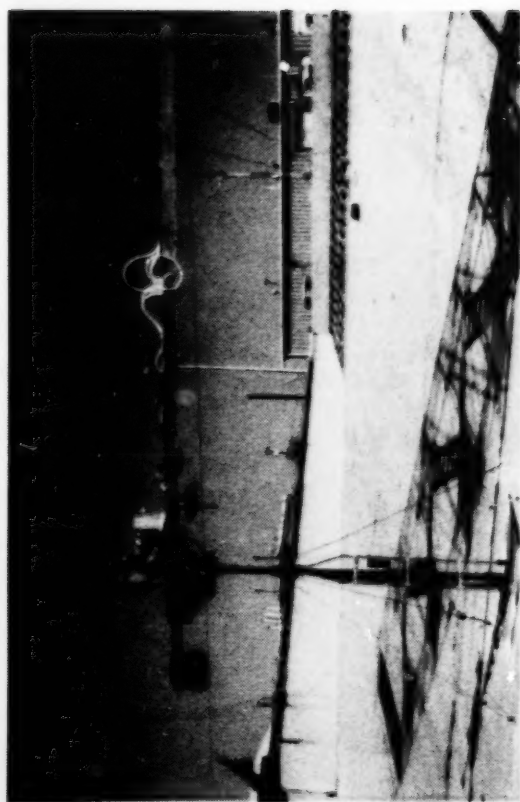
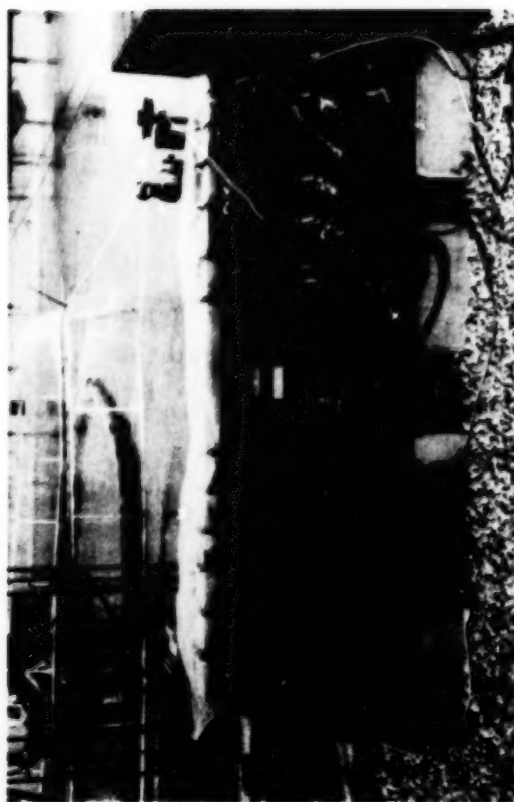
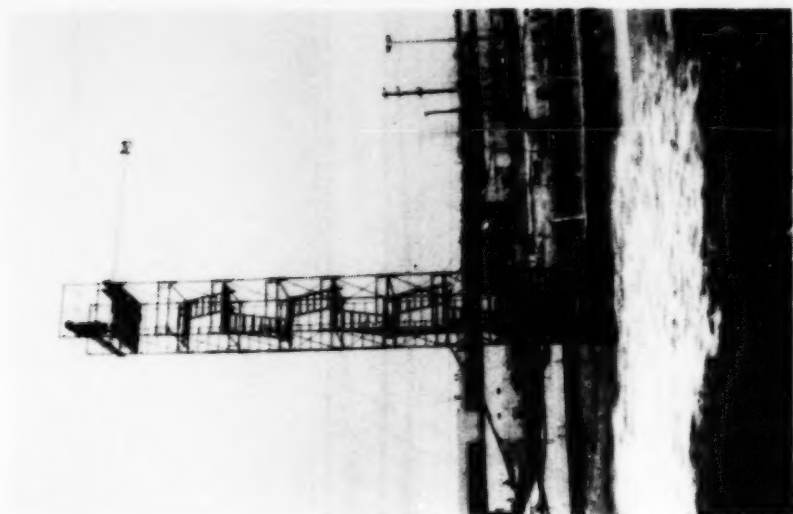
Observation Tower and Camera Boom

Figure 1

Rotating Spray Apparatus

Figure 3

Pump Module for Concentration
Measurements



Mackay et al (1986) have proposed that the effectiveness of a dispersant may be a function of the oil slick thickness or equivalently the D/O ratio. The proposed relationship does not appear to hold for the data of a recent report (Belore (1987)). In the course of this work, several attempts to measure the thicker oil of the slicks with an IR camera were unsuccessful but average dispersant/oil ratios for the thick oil areas were determined from 35mm photographs as described above.

A few tests were conducted with low salinities such as might be encountered in ocean bays where a river enters. Salinity would be expected to affect the dispersing process as the salt ions will interact with the hydrophilic ends of the surfactant molecules.

The Oil/Water Interface

Oil drops are formed at the oil/water interface when sufficient energy is transferred to the surface from the waves. In these tests several wave energies were used in hopes of elucidating some of the transfer mechanism. Most tests were carried out with regular waves of 10cm or 20cm height. These waves are described well by Stokes' 2nd order wave theory and have an energy slightly higher than the peak in the energy spectra of typical ocean waves (U.S. Army (1973)). A few tests were carried out with computer generated waves which had the 'Joint North Sea Wave Project' (JONSWAP) spectra (Pierson and Moskowitz (1964)). The parameters required to generate these spectra were obtained from Beaufort Sea wave data and should produce waves representative of that area.

For a given wave energy, a more effective dispersant might create more small oil drops in the water. A dispersed oil cloud with a proportionately smaller drop size distribution should circulate more quickly through the water and resurface more slowly because of a lower Stokes rising velocity. In many of the wave basin tests, samples of the dispersed oil cloud were regularly analyzed with a particle size counter. Oil drop sizes in the range of 1 to 20 microns were determined with a Hiac/Royco Model 4100 counter attached to a Model 346 laser sensor.

Dispersed Oil Circulation

The effectiveness of a dispersant can be determined either by measuring the amount of oil remaining in the slick at a given time or by measuring the amount of dispersed oil in the water. In all of the wave basin experiments, the concentration of oil in the water column has been monitored as a function of time. Typically, six Turner Design Model 10-005 fluorometers have been used with a series of pumps to continuously monitor up to 12 sample locations throughout the basin. The pump module is shown in Figure 3. The data from the fluorometers was digitized and stored on floppy disks in real time.

At the end of each experiment (usually three hours), any oil remaining in the containment boom was collected with a disk skimmer. The oil and water collected was allowed to separate overnight and then oil-in-water and water-in-oil determinations were made.

RESULTS AND DISCUSSION

Results from some of the more recent basin experiments are summarized in Tables 1 and 2. The dispersant effectiveness shown was determined from the oil remaining after the experiment was over, with appropriate corrections for evaporative losses during the weathering of the oil and during the experiment itself. Other results from these and additional tests not summarized in the tables are discussed in the sections following.

Dispersant Application

With one exception, the dispersant to oil ratio was intended to be 0.05 in all of the tests reported here. In the most recent tests with the rotating arm sprayer, it was possible to measure the D/O ratio by measuring the thick (non-sheen) oil areas from overhead photographs of the slick taken during the spraying operation. An image processing system on an IBM-PC was used for the area measurement. These results are listed in Table 2. In the four instances where the D/O ratios are particularly low, the oil had spread across the containment boom in a very irregular patchy slick, and the spray operator had some difficulty in hitting only the thicker oil.

For the tests reported in Table 1, a simple overhead spray bar with no remote control, or a hand-held sprayer were used. No photographs from directly above the slick were available for image analysis. Only estimates of the D/O ratios could be made from videos of the spraying operation. When the hand sprayer was used (from a boat), all of the dispersant was applied to the oil.

The estimated and measured D/O ratios using overhead spray equipment indicate that dispersant application from the air can lead to significant under treatment of the oil slick. In comparable experiments (e.g.: 2 and 9, 4 and 5, 19 and 21), the dispersant effectiveness was always lower when the D/O ratio was lower. The effectiveness appears to decrease if the D/O ratio is below about 0.030.

Dispersant/Oil Interaction

When an oil was weathered in situ, a sample was taken from the slick just prior to dispersant application. A simulated distillation of the sample was then obtained by gas chromatography. Points from the distillation data were compared to points on distillation curves of samples of the same oil which had been weathered by known amounts. An example of the calibration 'weathering' curve for Norman Wells Oil is shown in Figure 4. If a sample of weathered oil lost 40% by weight at a temperature of 250°C, then the calibration curve for that distillation temperature shows that the true weight loss by weathering was 16%. Similar calibration curves were measured for each oil used in the dispersant tests.

The diffusion of a dispersant through the oil to the oil/water interface will likely be affected by the oil viscosity. If the measured dispersant effectiveness is compared in otherwise similar tests (1 and 2, 9 and 11, 6 and 7), the effectiveness is seen to decrease with increasing weathering or viscosity. Laboratory studies show a similar trend.

TABLE 1 DISPERSANT EFFECTIVENESS

TEST OIL	DISPERSANT	WEATHERING (%)	VISCOSITY ² (cST)	SALINITY (ppt)	WAVE TYPE	ESTIMATED ¹ D/O	EFFECTIVENESS
1	COR 9527	35	240	28	REGULAR	0.03	39
2	COR 9527	FRESH	10	28	20 cm	0.03	53
3	CRX-8	(5-10)	↓	31	10 cm	0.04	15
4				30	20 cm	0.02	28
5				30		0.05	77
6	COR 9550	23	46	29		0.05	42
7	COR 9550	FRESH	10	31		0.05	55
8	CRX-8	18	40	30		0.05	76
9	COR 9527	FRESH	10	29		0.05	77
10	NO DISP	FRESH	10	28		0.00	1
11	COR 9527	35	240	28		0.04	43
12	COR 9550	FRESH	10	1		0.05	27

1. NOMINAL RATIO: D/O = 0.05

2. APPROXIMATE VALUE AT 0°C

TABLE 2 DISPERSANT EFFECTIVENESS

TEST	OIL	DISPERSANT	WEATHERING (%)	VISCOSITY ² (cST)	SALINITY (ppt)	WAVE TYPE	MEASURED ¹ D/O	EFFECTIVENESS (%)
13		COR 9527			14		0.019	41
14		COR 9527			24		0.040	59
15		CRX-8			24		0.045	63
16	NORMAN	EN 700			24	REGULAR	0.040	82
17	WELLS	CRX-8		10	30	WAVES	0.023	56
18	CRUDE	COR 9527	FRESH (5-10%)		31	20 cm	0.016	48
19		CRX-8			31	HEIGHT	0.038	87
20		COR 9527			30		0.029	86
21		CRX-8			30		0.020	56
22		EN 700			31			100
23		COR 9527		700	30		0.033	61
24	ALASKA	COR 9527		700	30	BEAUFORT	0.023	63
25	NORTH	COR 9550		1700	30	H _S =20 cm	0.043	60
26	SLOPE	COR 9527		700	30	H _S =10 cm	0.048	42
27		COR 9550			30	H _S =20 cm	0.043	53
28		EN 700			30	H _S =20 cm	0.040	38

1. NOMINAL RATIO: D/O = 0.05 except in TEST 21 where D/O = 0.020

2. APPROXIMATE VALUE AT 0°C

Figure 4 WEATHERING OF NORMAN WELLS OIL

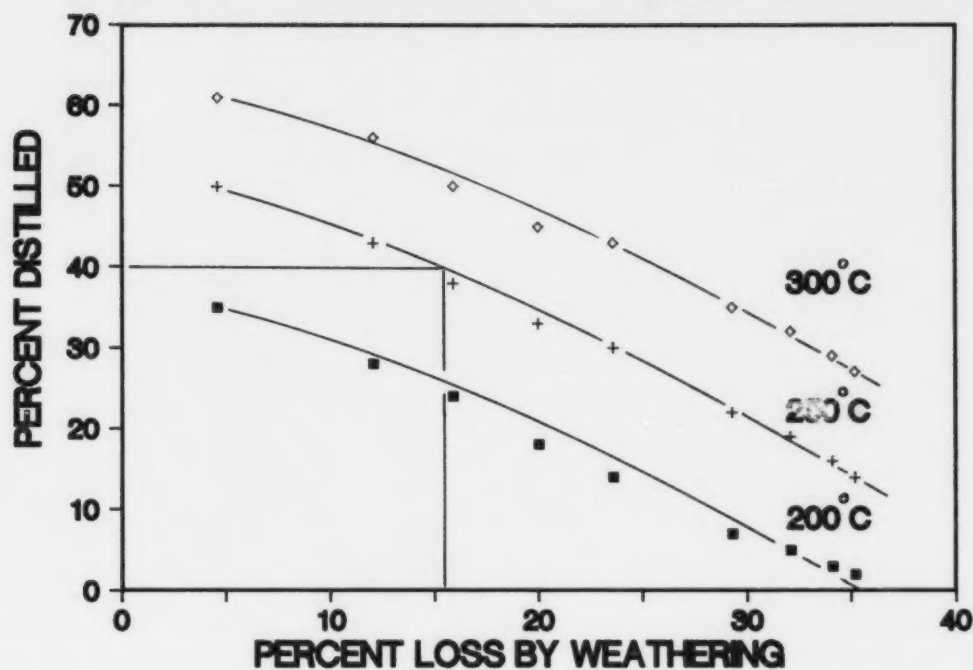
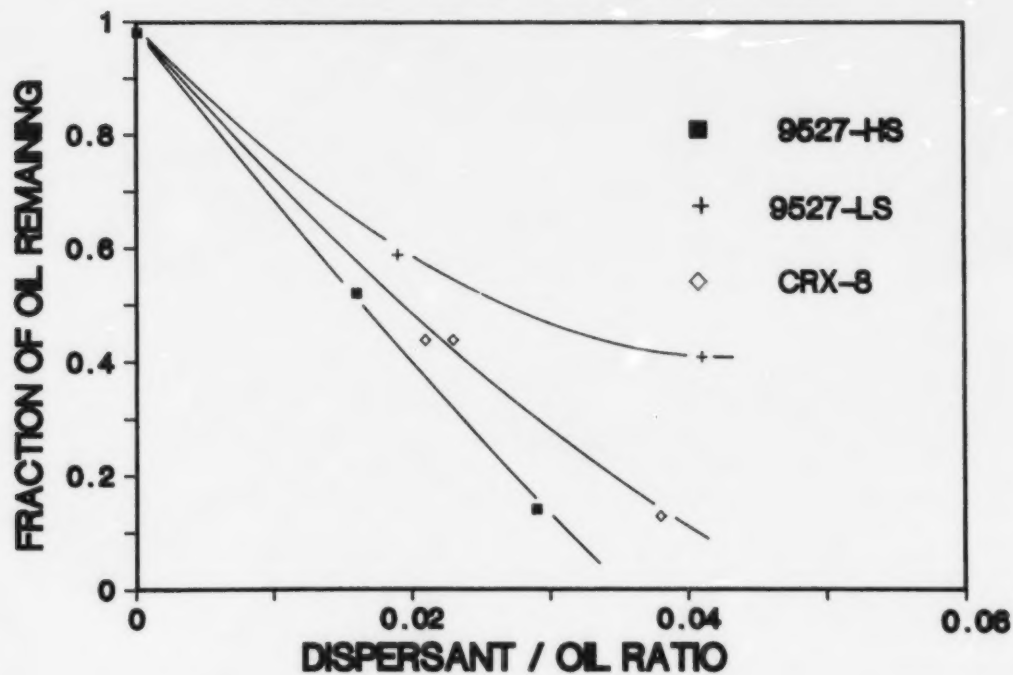


Figure 5 MACKAY MODEL TEST



For a few instances of comparable tests, the measured D/O ratios have been plotted in Figure 5 as a function of non-dispersed oil. The ratios are the average values measured on the thick portion of the slick. The dispersant spray parameters remained constant during these tests but spray drop size distributions were not measured. It is interesting that the curves appear to agree with the Mackay model at least for thick oil slicks. Corexit 9527 has been blended for sea water and, as the figure shows, is less effective at lower salinities.

The Oil/Water Interface

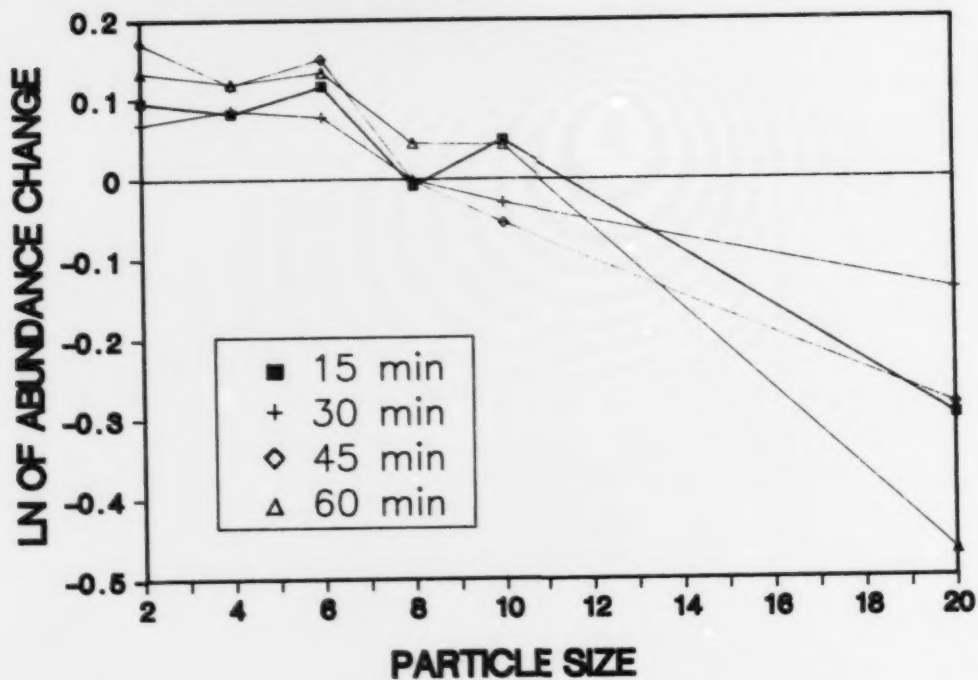
The experimental conditions, except for wave energy, were similar in tests 3 and 5 and tests 24 and 26. In each case a lower wave energy resulted in a lower dispersant effectiveness. This can be attributed to a combination of differences in the oil drop size distribution immediately beneath the slick and to differences in the wave orbital motion which circulates the oil drops. Changes in the oil drop size distributions 50cm below the slicks, as a function of time, for tests 24 and 26 are shown in Figure 6. The graphs show the relative changes in the distributions compared to the distribution before the dispersant was applied. The zero baseline represents the distribution before the experiment. Positive values mean the abundances of that drop size have increased, while negative values mean the abundances have decreased, relative to the beginning of the experiment. In test 24, more of the smaller drops were detected 50cm below the surface during the first hour after the dispersant was applied. This implies that the dispersant and wave energy combination produced a large number of small drops which were easily circulated through the water column. In contrast, the same dispersant with a lower wave energy produced a drop size distribution with decreased numbers of small drops. In test 26 the significant wave height (H_g) was 10cm compared to 20cm in test 24. Dispersant effectiveness was higher in test 24 which had the drop distribution with the relatively smaller sizes.

Dispersed Oil Circulation

In order to measure dispersant effectiveness in an ocean spill, either the oil dispersed in the water column or the oil remaining on the surface must be measured as a function of time. At present, there are no accurate means of measuring oil slick thicknesses over large slick areas and consequently, measurements of the dispersed oil in the water are used in attempts to determine dispersant effectiveness. In wave basin experiments where the volume of water is large but limited, it should be possible to monitor dispersed oil movement and to determine average oil concentrations.

During the course of our experiments we have used fluorometers in a variety of sampling scenarios in attempts to adequately follow dispersed oil movement. These have usually included six instruments connected to as many as 12 sampling locations throughout the wave basin. Computer models of the oil flow through the basin have been used to help determine sampling locations for the fluorometers (To et al (1987)). Two typical examples of the concentration data from the fluorometers are shown in Figure 7. In the upper diagram, the outputs of four fluorometers are shown for test 23. Note that the curves are offset at time zero to improve visibility. The lower diagram shows similar outputs for test 27. A number of observations can be made from such diagrams. Usually oil concentrations under the slick rise dramatically within 10 to 15 minutes of dispersant application and then slowly decrease over an hour or so. Most dispersant activity seems to finish within the first hour.

Figure 6
NORMALIZED PARTICLE SIZE - TEST 24



NORMALIZED PARTICLE SIZE - TEST 26

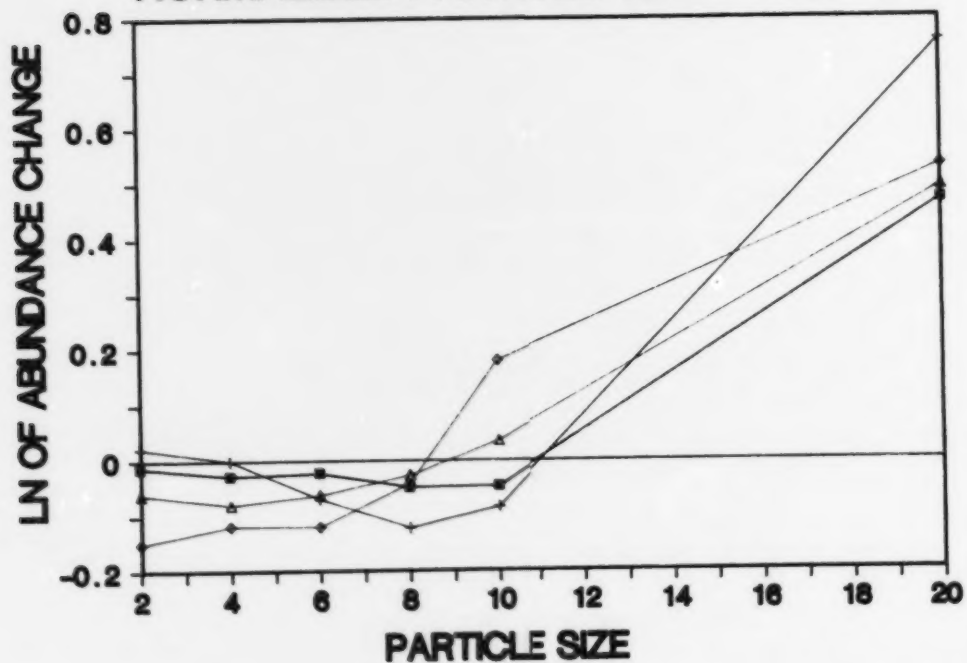
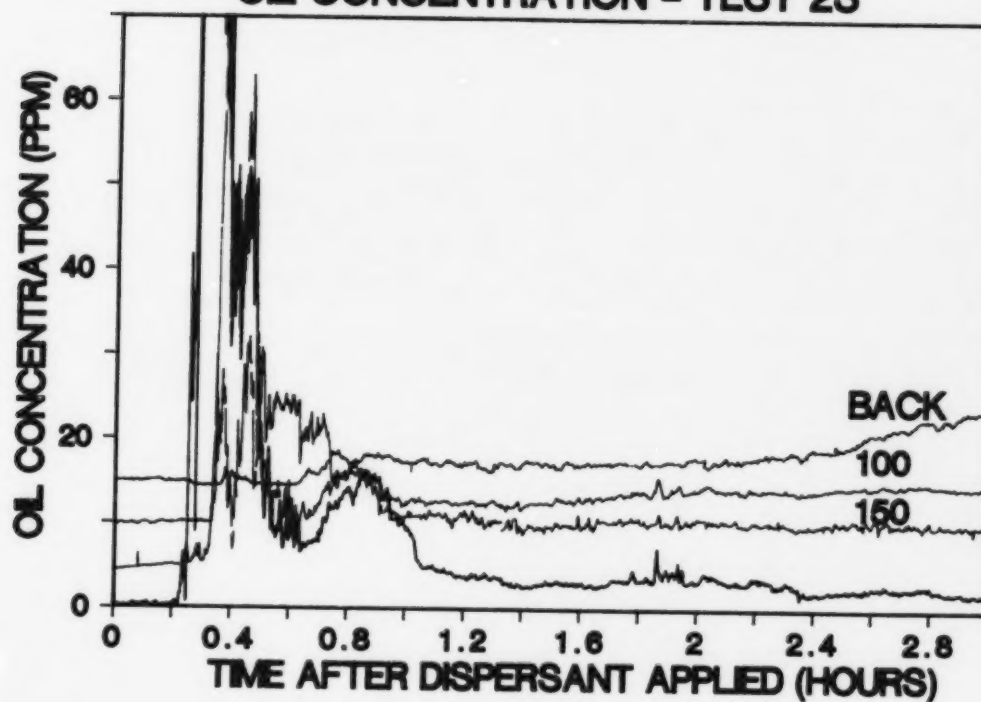
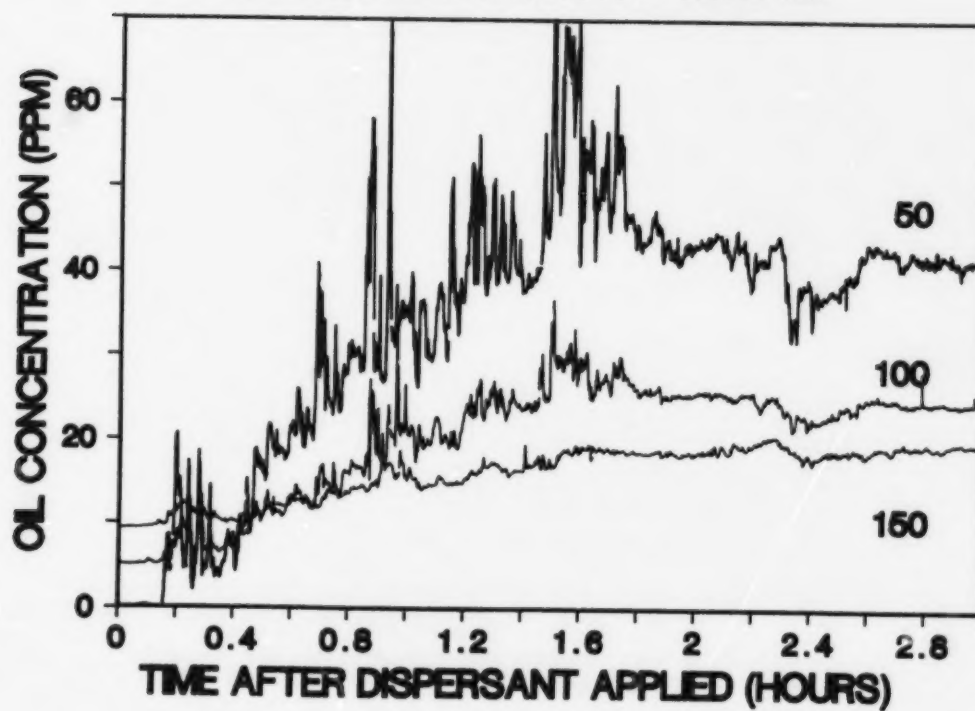


Figure 7
OIL CONCENTRATION - TEST 23



OIL CONCENTRATION - TEST 27



Peak oil concentrations decrease with increased depth below the slick and background concentrations slowly increase with time. The lower diagram is more unusual. The dispersant used in this test appears to produce larger oil drop sizes which circulate through the water at a slower rate.

A study of many such concentration curves in combination with photographs of the water surface has shown that dispersed oil clouds can be very concentrated and very inhomogeneous (Brown et al (1987)). The dispersed oil movement is dominated by small water currents rather than diffusion. Consequently, it is very difficult to measure dispersed oil volumes even on the basis of frequent closely spaced concentration measurements. In basin experiments, the dispersant effectiveness has most easily been determined by measuring the oil left in the containment boom at the end of the experiment. These results suggest that it will be very difficult to estimate dispersant effectiveness in ocean spills from dispersed oil concentrations.

SUMMARY

Over a four year period approximately 40 oil spill experiments have been conducted in a large wave basin. Many measurements have been made to follow the movement of the oil from the slick, including extensive fluorometric concentrations, oil drop size distribution determinations, and large numbers of photographs. Some of the conclusions of this work are:

- o Good dispersant application to the thick oil is critical for effective dispersion. Dosage rates should be > 0.03 D/O.
- o Dispersants can be over 80% effective even in water below 5°C.
- o Although effectiveness decreases with viscosity, 60% dispersion can be achieved with a viscosity of ~ 1800 cSt.
- o Dispersion will occur at low wave energies but circulation of the oil in the water is very slow.
- o Dispersed oil plumes are very inhomogeneous so that effectiveness measurements on the basis of oil in water concentrations are difficult.
- o Dispersant effectiveness must be defined as a function of time.
- o Dispersants appear to be most active in the first 30 to 60 minutes after application.
- o More effective dispersants produce smaller oil drops in the water.

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